Isotope study of moisture sources, recharge areas, and groundwater flow paths within the Christchurch Groundwater System

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in Geology at the University of Canterbury

By

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University of Canterbury

Frontispiece

Water dissolving and water removing
There is water at the bottom of the ocean
Under the water, carry the water
Remove the water from the bottom of the ocean
Water dissolving and water removing

Letting the days go by, let the water hold me down
Letting the days go by, water flowing underground
Into the blue again, into the silent water
Under the rocks and stones, there is water underground

-David Byrne

Abstract

Determining sustainable water resource utilization rates is an important problem faced by regulatory agencies all around the world. One of the key parameters in determining accurate water budgeting schemes is the rate of water resource replenishment, or 'recharge' in groundwater systems. Fundamental questions regarding groundwater recharge include: What is the source of recharge? What is the spatial distribution of recharge? What is the annual average recharge rate, from potentially disparate sources in disparate areas? Answers to these questions can be gained through combining physical and chemical hydrogeological research tools, including stable isotopic compositions.

Land-use intensification, including significant increases in dairying, has placed a priority on developing water resource management practices throughout New Zealand. Here we present the first compilation of $\delta^{18}O$ and δD values from individual precipitation events, local surface waters, depression springs, and groundwaters from the greater-Christchurch area. A variety of analytical methods were used in an effort to evaluate the potential use of stable isotopic compositions as tracers of surface-groundwater interaction in the local hydrologic cycle.

The results of this thesis found the isotopic variability of Christchurch precipitation to be highly varied. Back-trajectory analysis of single precipitation events exhibit pathways arriving from three principal sources: the Southern Pacific Ocean, the Tasman Sea, and the Tropical Pacific Ocean. Separately, $\delta^{18}O$ and δD values from these sources show three distinct local meteoric water lines, which are determined to be largely affected by the environmental conditions present in these areas at the time water vapour formation. Intra-storm variation of extra-tropical cyclones support these findings as significant changes in deuterium excess as moisture sources change with southward movement of the low pressure system.

Three line-conditioned tests were subsequently developed to compare the relationship between monthly surface rainfall, surface water, and groundwater samples to the respective moisture origins. Surface rainfall, rainfall infiltration, surface waters, and groundwaters all exhibit the least amount of deviation from the Southern Pacific Ocean local meteoric water line. These observations suggest the principle moisture source to Christchurch to be from

west-south westerly flow from the mid-latitudes. However, these similarities do not make partitioning their relative contributions to the groundwater system easy.

Previous physical and isotopic investigations have shown the dominant sources of recharge to the Christchurch Groundwater System (CGS) are alpine rivers and local precipitation of which there is statistically significant difference with respect to $\delta^{18}O$ values. A binary single-isotope mixing model allows for quantification of the relative contributions of alpine river and precipitation derived inputs to local depression springs. The isotopic model indicates that approximately 80% of spring discharge was derived from alpine rivers, in good agreement with recently published physical mass balance model results. Deep groundwater flow paths however show groundwater to flow from the Central Canterbury Plains to the CGS. Potentially including losses from the upper Waimakariri River reaches. If included, this places a net recharge amount to the CGS water budget, which if using losses from only the lower Waimakariri River, there is a net loss. Losses from the upper reaches and subsequent groundwater flow into the CGS are likely as there have been no observed declines in groundwater levels even though there is currently a net loss by only using recharge components within the CGS. Ultimately, recharge from groundwater movement from the Central Canterbury Plains may play significant role; however, a much more sophisticated geochemical model is needed to test these theories and determine contributions. This research demonstrates the utility of stable isotopes as tracers of hydrogeological processes, particularly in shallow groundwater, and their potential contributions to the water resource allocation decision making process.

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Chapter 1 : Introduction

1.1. Global Significance of Water Resources Research

Fresh water is critical to both sustaining the quality of humankind and terrestrial ecosystems (Schrader and Blackstock, 2010; Shanton, 2009; Seiler and Gat, 2007). At present, there is an unprecedented demand on water resources on a variety of spatial scales, with many current extraction rates greatly exceeding the rate of natural replenishment (UNEP, 2008). As hydrologic stresses are expected to increase in the future from both increased demand and potential climate change (Bates et al., 2008), determining sustainable water resource utilization rates is an important problem faced by human populations the world over. Clearly, these utilization/allocation rates must be based on accurate scientific analyses (Narasimhan, 2009).

1.2. Groundwater: a Global Perspective

Groundwater (Figure 1.1) is the second largest freshwater reservoir on Earth, after cryospheric reservoirs, with an estimated volume of 7.5×10^6 km^3 (Berner and Berner, 1987). As a water resource, groundwater is clean and cost-effective, particularly in semi-arid to arid areas limited by surface water resources, such as northern Africa where water extraction is dominantly from groundwater (Bovolo et al., 2009) for which two billion people rely on groundwater as their primary source of water (Kemper, 2004).

Hydrologic fluxes from groundwater systems to surface water bodies are also significant to aquatic and terrestrial ecosystems. For example, groundwater can maintain baseflow in rivers and streams, which can be integral components of sensitive ecosystems across the planet (Tharme, 2003; Bovolo et al., 2009). Conversely, surface waters can also be crucial sources of groundwater replenishment, particularly in areas where evaporation rates exceed precipitation rates, like Canterbury, New Zealand, California Basin, USA, and Central Australia (Talbot and Bowen, 1986; Criss and Davisson, 1996; Vanderzalm et al., 2011).

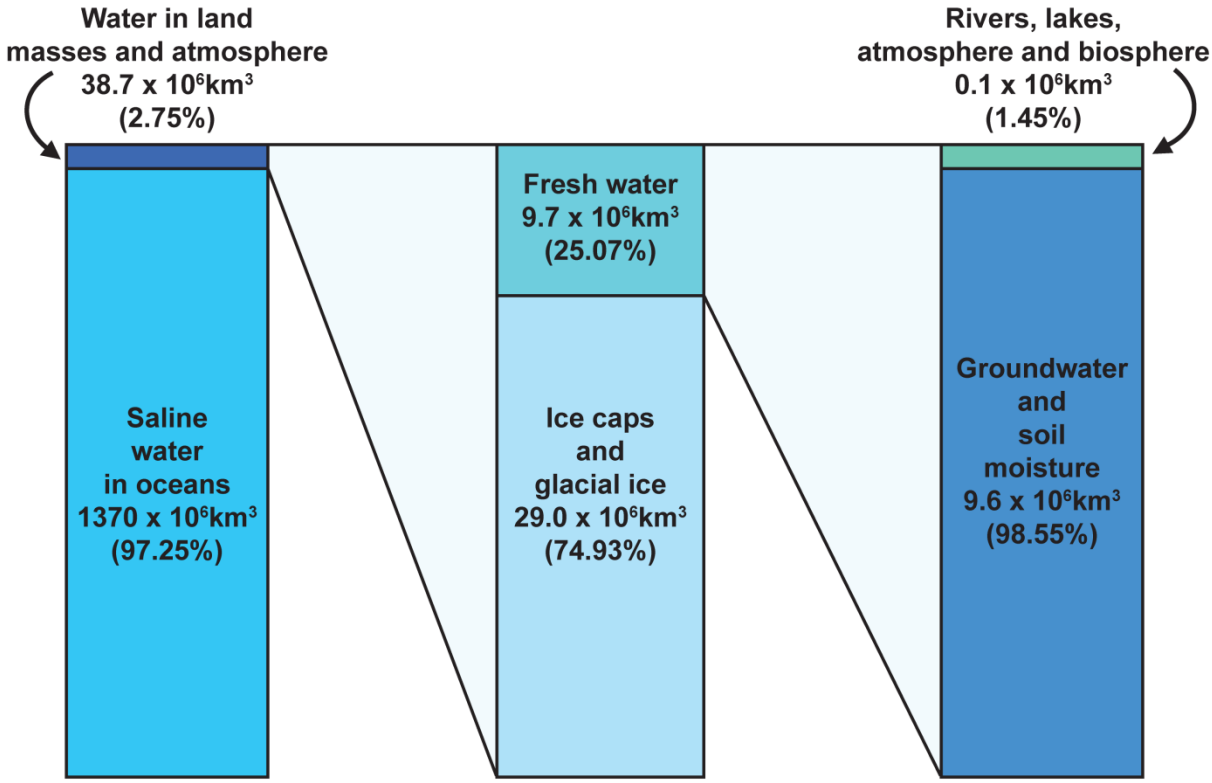

Figure 1.1: Distribution of global freshwater resources and estimated volumes (modifed from Bemer, 1987; Maurits la Riviere, 1989)

1.3. Groundwater and Surface Water Resources of New Zealand

In the most general terms, New Zealand has an "abundant" water supply (Waugh, 1992), due to high precipitation rates, runoff, and relatively high storage volumes from natural hydrologic reservoirs including snow, ice, and groundwater. Estimated average annual stationary volumes of freshwater in New Zealand total 2.1 x 10^3 km^3/year (Table 1.1). Of this, approximately 77% (1.7 x 10^3 km^3) is present as groundwater (Toebes, 1972). However, the distribution of and occurrence of freshwater storage varies greatly with changes in geology and climate (White, 2001). Furthermore, the relative "abundance" of freshwater volumes will vary depending on the magnitude of local hydrologic stresses (i.e. abstractions and climate change) (Narasimhan, 2009).

In general, water resources in New Zealand have primarily been utilized for hydro-electricity generation, irrigation, municipal, and private water supplies (Waugh, 1992). Mosley (1988) estimated the total value of freshwater sources in New Zealand to total approximately 2.3 billion dollars per year (NZD). White (2001), however, estimated this resource to be between 24 and 25 billion dollars per year (NZD). Regardless, demand for both surface and

groundwater is set to increase with agriculture shifts to land and water intensive dairying and continuing industrial development, including potential lignite exploration.

Hydrologic Reservoir	Average Annual Stationary Volume (km^3)
Ephemeral Snow	7.7
Permanent Snow and Ice	50
Interception Storage	1.8
Lakes	405
Channel Storage	13.3
Groundwater (baseflow)	1392
Deep Groundwater	265
Biological Storage	0.27

Table 1.1: Average stationary volumes of freshwater storage across New Zealand (modified from Toebes 1972)

1.4. Water Use in Canterbury and Christchurch

At the regional scale, Canterbury is by far the largest consumer of groundwater resources in New Zealand (~ 250 m^3/s or ~ 7.9 km^3/year) (Table 1.2) (Lincoln Environmental, 2000). The second largest consumer is Otago (~90m^3/s).The major use of groundwater in Canterbury is for irrigation (~ 85%), and current allocation rates in many parts of Canterbury exceed the annual recharge derived from their respective recharge sources (Kerr et al., 2003; White et al., 2003).

Urban areas in Canterbury also rely on groundwater resources. The sole source of public reticulated water to Christchurch City is derived from groundwater. The source of this groundwater is aquifers just below Christchurch hereby after referred to as the Christchurch Groundwater System (CGS). Average annual abstractions from the CGS are ~ 104 x 10^6 m^3/year (~ 0.1 km^3/year) (Talbot, 2010). Yet, characterizing the sources and amounts of annual replenishment to the CGS aquifer system has proven to be a difficult task (Little, 1997; Brown, 2001).

			Percent Use of Groundwater		
Region	**Total Allocated**	**Groundwater Allocated**	**Irrigation**	**Industrial**	**Community**
Northland	7.9	0.3	64	18	18
Auckland	8.1	2.8	43	19	38
Waikato	10.3	4	13	59	28
Bay of Plenty	8.9	2.6	57	3	40
Gisborne	1.4	0.4	91	0	9
Hawke's Bay	16.8	11.3	66	15	19
Taranaki	3.4	0.1	25	50	25
Manawatu-Wanganui	5.2	2.9	32	26	41
Wellington	9.8	4.6	51	6	43
Tasman	6.7	4.2	85	5	10
Marlborough	8.2	5.8	75	15	10
Canterbury	249.8	82.4	85	3	12
Otago	90.1	4.9	33	33	33
Southland	2.4	0.6	20	28	52

Table 1.2: Total water and groundwater allocation allocations by region across New Zealand and percent uses for allocated groundwater. Canterbury is highlighted (Lincoln Environmental, 2000)

Land-use intensification has placed a priority on developing water resource management practices throughout New Zealand. However, accurate quantification of recharge, identification of groundwater flowpaths with depth, and groundwater discharges remain elusive with estimates differing as much as 20% between both previous physical and chemical investigations (Taylor et al., 1989; Scott and Thorley, 2009; Talbot et al., 1986; Little, 1997). Ultimately, these large uncertainties contribute to the significant ambiguity associated with resource allocation in the CGS, which are critical concerns with respect to groundwater characterization and management (Peters, 1994).

1.5. Thesis Objectives

The overarching goal of this thesis was to quantify groundwater recharge rates in the CGS using stable isotope geochemistry. Prior isotope investigations in the Canterbury region are limited by the lack of knowledge regarding the stable isotopic variability in local

precipitation at the event scale. This data is fundamental in determining moisture sources and characterizing end-member groundwater compositions from synoptic precipitation events that, cumulatively, constitute rainfall infiltration to groundwater recharge (Craig and Gordon, 1965; Clark and Fritz, 1997; Gat, 1996; Friedman et al., 2002; Criss and Davisson, 1996).

Additional objectives of this thesis include:

1. Characterization of the isotopic variability of precipitation occurring over Christchurch, New Zealand, including the interpretation of these data in the context of:
    a. Global datasets of stable isotopes in precipitation
    b. Determination of source region and effects along air parcel pathway
    c. Local meteorological conditions during sampling periods
    d. High-alpine derived rivers
2. Quantify recharge contributions to shallow groundwater in the CGS from rainfall infiltration and high-alpine derived rivers using a single-isotope binary mixing model
3. Comparison of groundwater chemistry at with groundwater flow nets generated for aquifers in the CGS

1.6. Thesis Format

This thesis is presented in 8 Chapters. Chapter 2 presents background information on basic concepts associated with the study of hydrology, hydrogeology and the applications of stable isotopes in hydrology. Chapter 3 presents a general review of the Central Canterbury Plains and the Christchurch Groundwater System with respect to geology, hydrogeology, and climatic regime of the South Island and the Christchurch Groundwater System study area. Chapter 4 reviews the methodologies undertaken for the various analytical, hydrological, and geochemical modelling used in this study. Chapters 5 presents the results for both physical and stable isotope variations regarding precipitation events collected in Christchurch from May 2009 through June 2010. This chapter also includes a more specific analysis of physical and stable isotopic variations associated with rainfall collected during two land falling extra-tropical cyclones over Christchurch. Chapter 6 presents stable isotope values for cumulative surface rainfall, rainfall infiltration, the Waimakariri River, and groundwater in the CGS. These data include original analyses undertaken for this thesis and previous studies. Chapter 7 presents a discussion of the results from Chapters 5 and 6 within the framework of the local Christchurch Groundwater System, which includes precipitation, surface waters, and

groundwater (atmospheric and hydropsheric fluxes). This chapter concludes with a new conceptual model of recharge for the Christchurch Groundwater System. Chapter 8 presents the final conclusions and implications of this study and highlights future areas of potential research.

Chapter 2 : Stable Isotope Hydrology

2.1. Introduction

Water moves through the various components of the earth system via the hydrologic cycle. This chapter presents an overview of the hydrological cycle and associated key concepts (i.e. water cycle, water fluxes between water reservoirs, physical continuity equation, etc.), in addition to a review of basic hydrogeological and fundamental stable isotope principles. These principles are relevant to tracing waters throughout the hydrological cycle. Emphasis is placed on the hydrogeological problems of surface water/groundwater interactions and the application of a single-isotope binary mixing model used for thesis is presented.

2.2. Hydrologic Cycle and Catchment Hydrology

Modern hydrology is said to have its beginnings with the seminal study made by Perault (1674), whereby quantifying precipitation totals in the upper catchment of the Seine River, France and relating these to streamflow (Dooge, 2011). In a broad sense, hydrology is the study of both the occurrence and movement of water between different reservoirs in the hydrosphere, collectively called the water cycle (Figure 2.1) (Shanton, 2009). For each of the reservoirs in, there is also an approximate estimate of volumes associated with various fluxes (i.e. evaporation, precipitation, etc.). Only one-third of continental precipitation derives from moisture directly associated with an oceanic moisture source leaving the remaining two-thirds to be derived from continental moisture fluxes (Figure 2.2) (Sharp, 2007). However, the global hydrologic cycle is a large-scale simplification of numerous processes that may vary from regional to local scales.

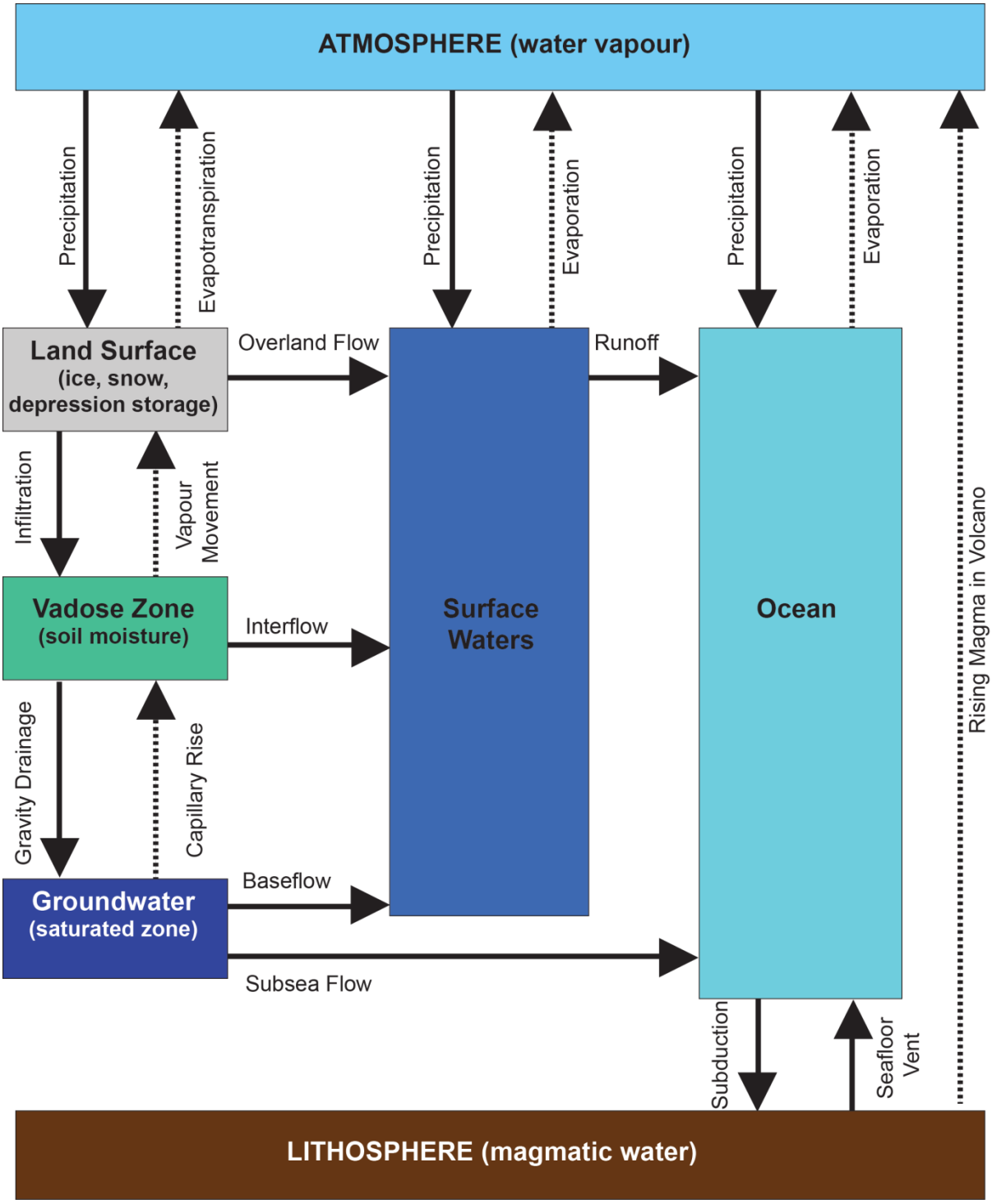

Figure 2.1: Conceptual model of the earth's near surface water cycle. Hydrologic reservoirs are represented by boxes and hydrologic fluxes between reservoirs are denoted by the arrows. Hatched lines indicate water vapour transport (Fetter, 2001)

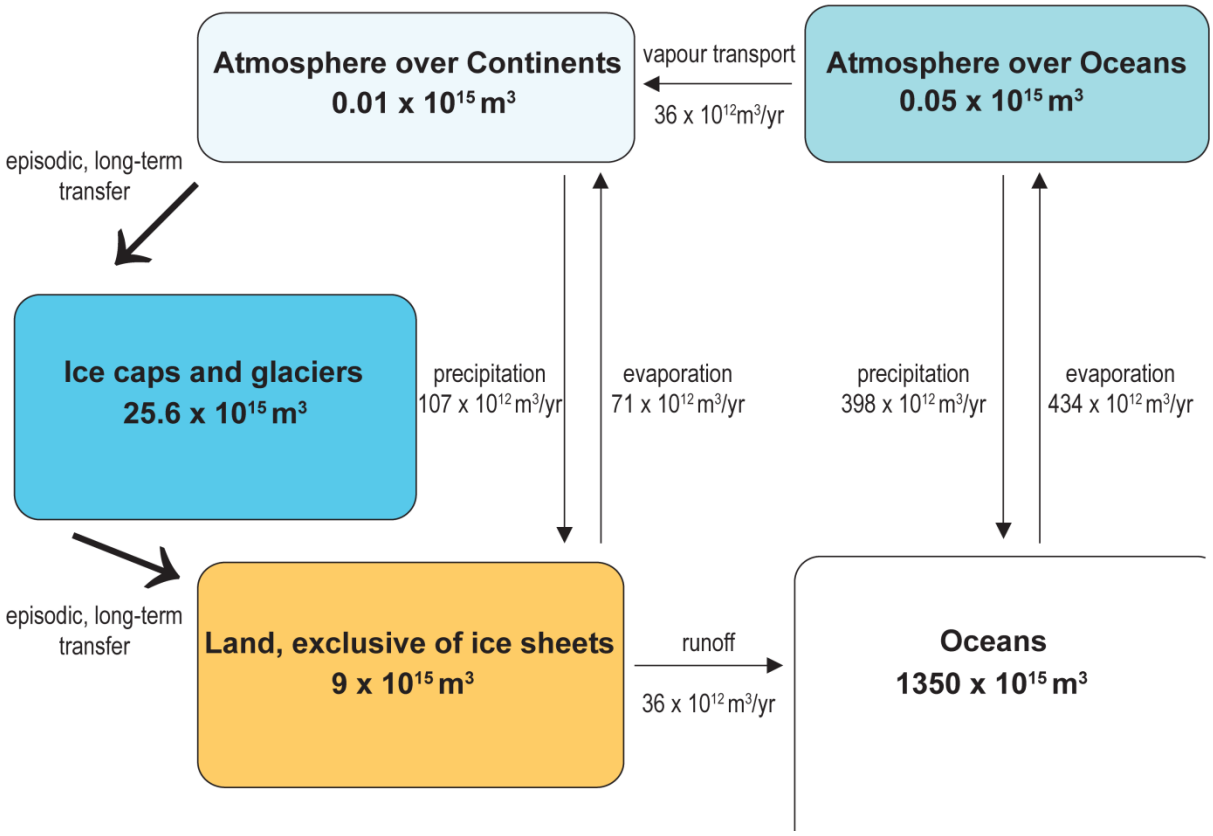

Figure 2.2: Fluxes between components of the hydrological cycle (Sharp, 2007)

A fundamental quantitative description of a system's water balance (whether a small river catchment, atmosphere, ocean, etc.) can be represented as:

$$P \pm E \pm \Delta S \pm Q = 0 \qquad \text{Equation 2.1}$$

Where P is precipitation; E is evaporation; ΔS is the change in storage and Q is runoff (Davie, 2008). Simplifying equation 2.1 yields

$$Q = P - E - \Delta S \qquad \text{Equation 2.2}$$

whereby for any system, or catchment, the sum of P, E, and ΔS is equal to Q. Equations 2.1 and 2.2 are both forms of the hydrologic continuity equation, which itself is simply a restatement of the law of mass conservation. Catchment hydrology is primarily focused on solving for these various parameters, particularly Q, within watersheds (Rodgers et al., 2005).

2.3. Hydrogeology

The study of hydrogeology is primarily concerned with the interaction of water and geologic materials (lithosphere) (Fetter, 2001). Groundwater is generally identified as the subsurface water occurring beneath the water table in saturated soils or geologic material for which it is present (Freeze and Cherry, 1977). As per this definition, groundwater may exist in a variety of geological settings (Figure 2.3).

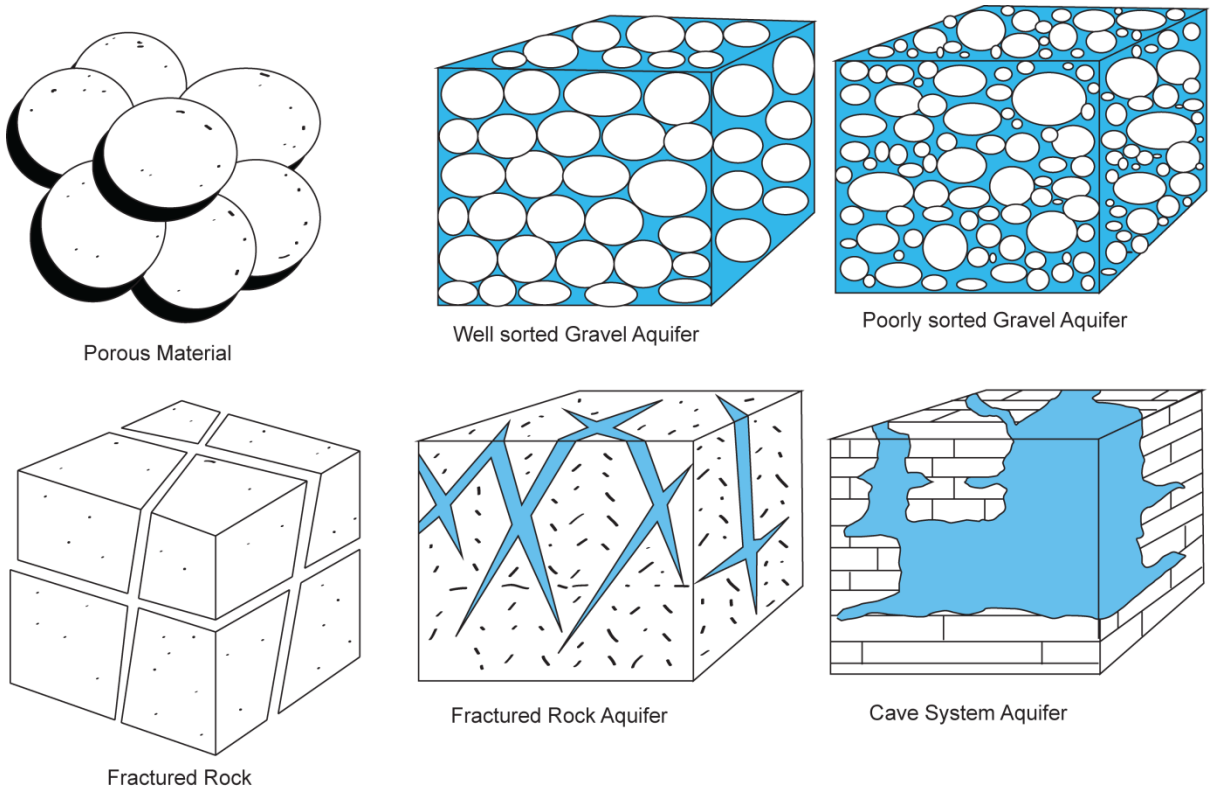

Figure 2.3: Groundwater may occur in both primary openings (i.e. porous material, such as gravels) and secondary openings (i.e. fractured rock, such as igneous and limestones). Examples of these openings on the aquifer scale could be a well-sorted or poorly sorted gravelly aquifer as on a river floodplain with respect to porous material or a basaltic aquifer occurring in fracture rock or limestone, or cave, aquifer system occurring in an karst environment (Heath, 1983).

2.3.1. Potentiometric Head and Potentiometric Surfaces

The volume of groundwater present in a given reservoir (i.e. aquifer) is controlled by the balance between groundwater recharge, volumes of storage, and discharge. The time that water spends in an aquifer system is referred to as the groundwater residence time. Aquifers are classed into three major groups: confined, semi-confined, and unconfined. Distinction between these three types arises from the presences of confining, or less permeable strata (i.e.

clay deposits) above and below more permeable sediments (i.e. gravels) in a groundwater system (Figure 2.4). Semi-confined aquifers simply represent the presence of less permeable sediments, but a distinct separation between hydrological units (i.e. aquifers and confining sediments) is not necessarily present.

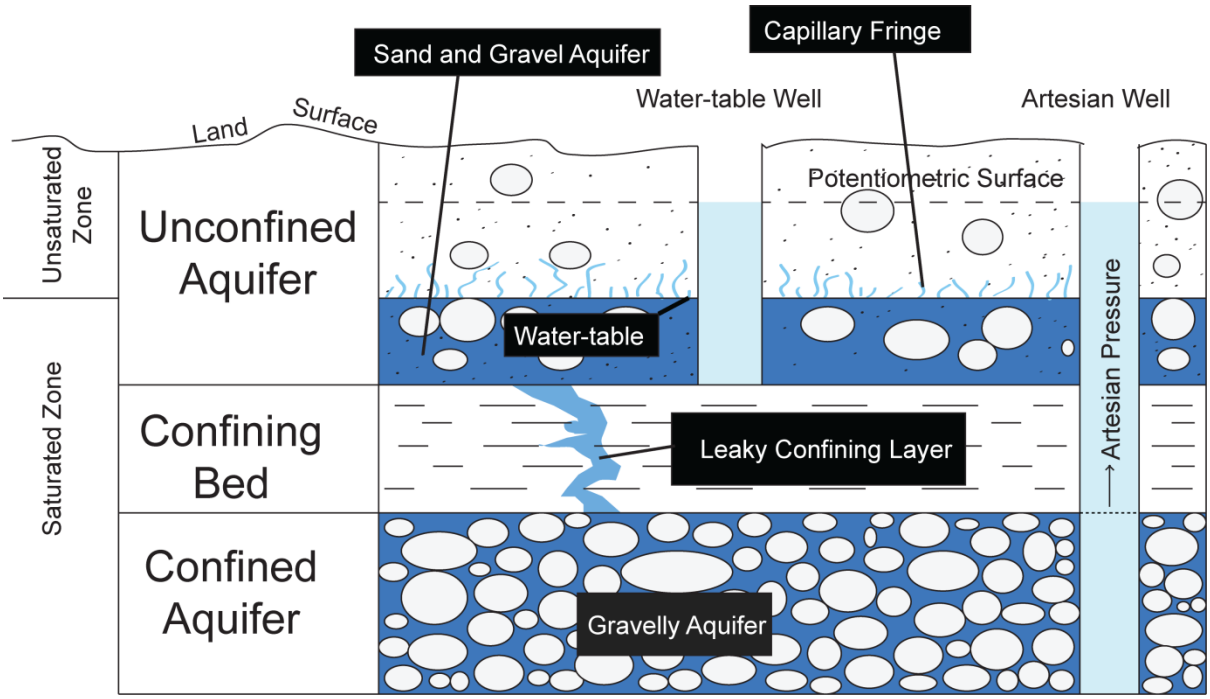

Figure 2.4: Aquifers may be classified as unconfined, semi-confined, and confined. The presence of a confining bed (less permeable units) is characteristic of a confined aquifer. These confining layers may not necessarily be impermeable where if water actively flows across through "confining" strata, confined aquifers are said to be leaky. Groundwater levels rising to and above the land surface are said to be 'artesian'. The saturated zone is defined by the depth where water is present throughout the pore spaces making up the geologic media of an aquifer system (Heath, 1983).

The potentiometric surface altitude, or hydraulic head, represents the altitude at which, given the pore pressure on the water within the geologic medium, is the altitude water would rest in a borehole or well. These altitudes can be above or below the ground surface. Compiling these observations potentiometric heads allow for the generation of potentiometric surfaces delineating the hydraulic gradient across a given region or specific aquifer. Notably, references to a 'water table' refer to the potentiometric surface of unconfined aquifers occurring at shallow depths (Figure 2.5). Such maps allow for the interpretation of groundwater flow as water will generally flow from higher groundwater levels to lower

groundwater levels, thus providing first-order observations of groundwater flow paths. These observations are critical for the validation of groundwater models (Alley et al., 2002).

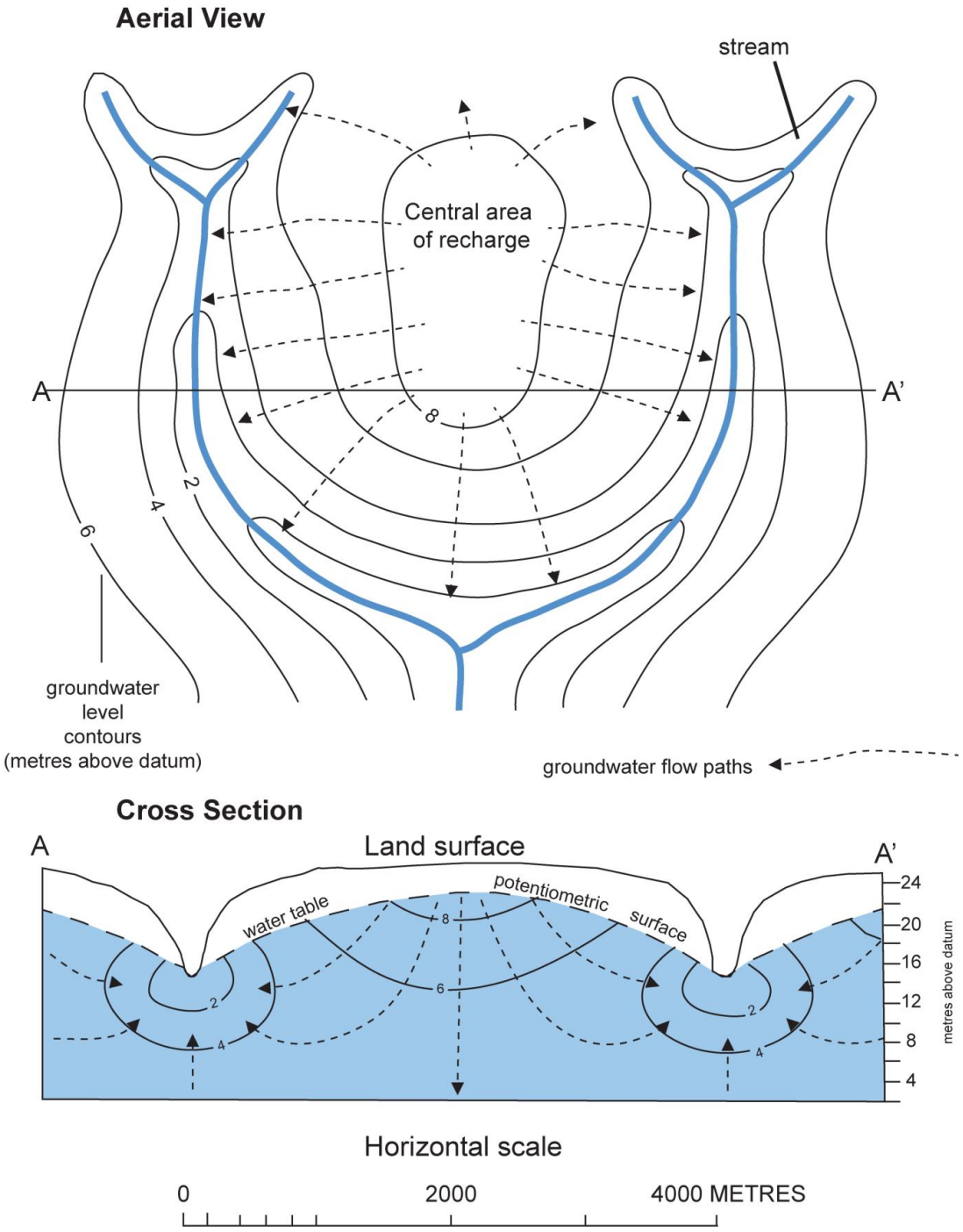

Figure 2.5: A critical observation of hydrogeology is that groundwater flows 'downhill' from higher to lower hydraulic heads as seen in the aerial view above. Groundwater flows perpendicular to the contours. In cross section, groundwater flow paths follow these same principles in terms of vertical movement, as well (Heath, 1983).

2.3.2. Groundwater Recharge

Groundwater recharge is characterized by the downward movement of water that reaches the water table. Recharge is sub-divided into diffuse or focused recharge types (Figure 2.6) (Healy and Scanlon, 2010). Diffuse, or local recharge, occurs over large areas generally as precipitation-derived rainfall infiltration flows downward through the unsaturated zone past the zero-flux plane (Allison, 1987). Focused recharge is associated with the movement of water from surface water bodies into groundwater systems. Focused recharge is further divided into localized recharge and indirect recharge (Lerner et al., 1990) whereby localized recharge is characterized by inflows from cracks, depressions, and joints and indirect recharge being characterized by inflow from mappable features (i.e. river) (Healy and Scanlon, 2010). In terms of groundwater use, determining groundwater recharge is a fundamental component in assessing viability and sustainability of groundwater resources. When groundwater abstraction volumes surpass natural rates of replenishment, reservoir volumes must decrease, which is referred to as groundwater mining or exploitation (Seiler and Gat, 2007). Although not always readily observable, exploitation of groundwater systems can lead to serious long-term consequences, which are not limited to, but may include decreases in aquifer storativity. A comprehensive review of flow, storage, and the short- and long-term effects of abstractions from groundwater systems is provided in Alley et al. (2002).

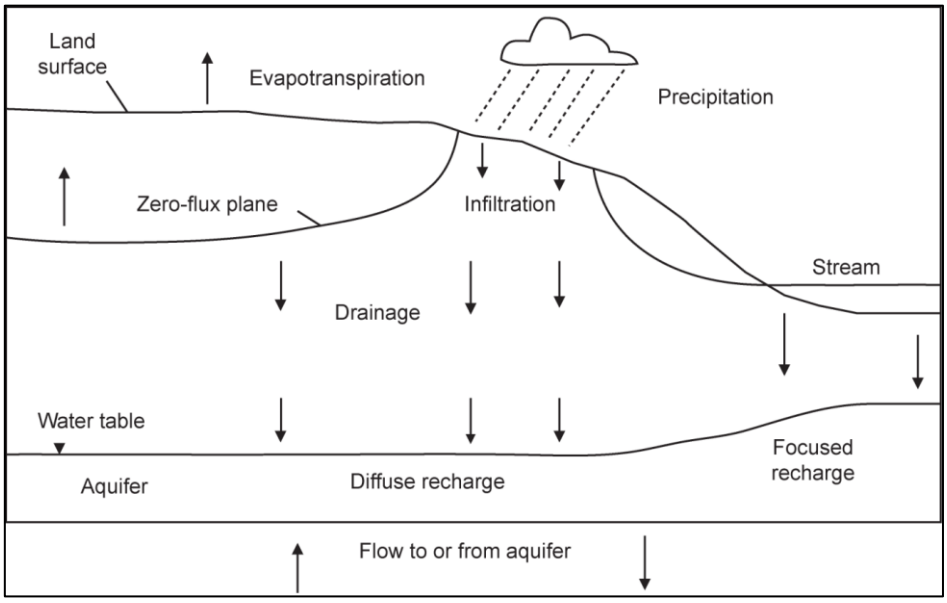

Figure 2.6: A schematic of processes associated with diffused and focused recharge (modified from Healy and Scanlon, 2010).

2.3.3 Groundwater Discharge

Groundwater discharge is simply characterized by the movement, or removal, of water from a groundwater system (Freeze and Cherry, 1977). Groundwater discharge occurs primarily as springs and as submarine discharge (i.e. discharge to rivers, lakes, and into the ocean). Other forms of discharge with specific reference to mass balance models also include groundwater abstractions.

2.3.4. Groundwater Residence Time

Groundwater residence times are defined by the average amount of time that water molecules spend in an aquifer system. Groundwater residence times begin with the entrance of water to an aquifer system via recharge processes (see section 2.3.2.) and subsequently end with the exit of water from the groundwater system via natural discharge processes or from groundwater abstractions by humankind (see section 2.3.3.). A simple mathematical representation of residence may be defined where:

$$\tau = \frac{V}{q} \qquad \text{Equation 2.3}$$

Residence time, τ, equals the volume of a system, in this case an aquifer, divided by the rate of flow through the aquifer, q. For example, Aquifer A has a volume of 5×10^6 m^3. The rate of inflows (recharge) and outflows (discharge) are both 10 m^3 per second for Aquifer A. Therefore, the rate of flow through the aquifer is 10 m^3 per second. Substituting these values for their respective parameters into Equation 2.3. yields a residence time of 1.0×10^5 seconds or ~ 1.2 days. Understanding the mean age of groundwater systems is critical in evaluating possible abstractions volumes in light of recharge and discharge rates from an aquifer system.

2.4. Stable Isotope Hydrology

Stable isotopes are widely used tool for tracing hydrologic fluxes within the water cycle. Stable isotope research has progressed dramatically since the suggestion of Briscoe and Robinson (1925) that isotopic fractionation could explain the variations in atomic mass observed in boron-bearing minerals. Specifically, stable isotope research began in the early 20th century with the discovery of the heavy stable hydrogen isotope deuterium by Urey et al. (1932). Over the past 80 years, a large number of studies have sought to understand both causes of stable isotopic fractionation and their utility as hydrological tracers. Table 2.1 summarizes the beginnings and early developments in modern stable isotope research from which it has evolved. From the outset, stable isotopic research has been applied to numerous

earth system components. Early applications of isotopes in hydrological problems focused primarily on tritium (^{3}H), the radiogenic isotope of hydrogen (Aggarwal et al., 2005). Although ^{3}H-dating remains a common method, stable isotope (δD and $\delta^{18}O$) proxies to hydrological problems has continued to expand from the 1960s onwards. These applications are now an integral component in the myriad methods relevant to deciphering process within the hydrologic cycle on a variety of spatial and temporal scales (Gat 2010).

Year	Title	Reference
1925	A redetermination of the atomic weight of boron	(Briscoe and Robinson, 1925)
1932	A hydrogen isotope of mass 2 and its concentrations	(Urey et al. 1932)
1935	Isotopic exchange equlibria	(Urey & Greiff 1935)
1935	The relative atomic weight of oxygen in water and air	(Dole, 1935)
1949	Natural variations in the isotopic content of sulphur and their significance	(Thode et al., 1949)
1950	Isotopic composition of oxygen in silicate rocks	(Baertschi, 1950)
1952	Variation in the relative abundance of carbon isotopes in plants	(Wickman, 1952)
1953	Deuterium content of natural water and other substances	(Friedman 1953)
1961	Isotopic variations in meteoric waters	(Craig 1961)

Table 2.1: Selected publications of early stable isotope research (modified from Sharp 2007)

2.4.1. Water Isotopes

Stable isotope hydrology centres on the relative abundances of the stable isotopes of hydrogen and oxygen. The stable isotopes of hydrogen (protium and deueterium) and oxygen (oxygen-16, -17, and -18) are shown schematically in Figure 2.7, excluding oxygen-17. Isotopes are atoms of a particular element with differing numbers of neutrons, as the number of protons within a nucleus is what defines the elemental species. Stable isotopes, in contrast

to radiogenic isotopes, do not exhibit spontaneous radioactive decay, however, possible; the probability of this occurrence is negligible (Sharp, 2007).

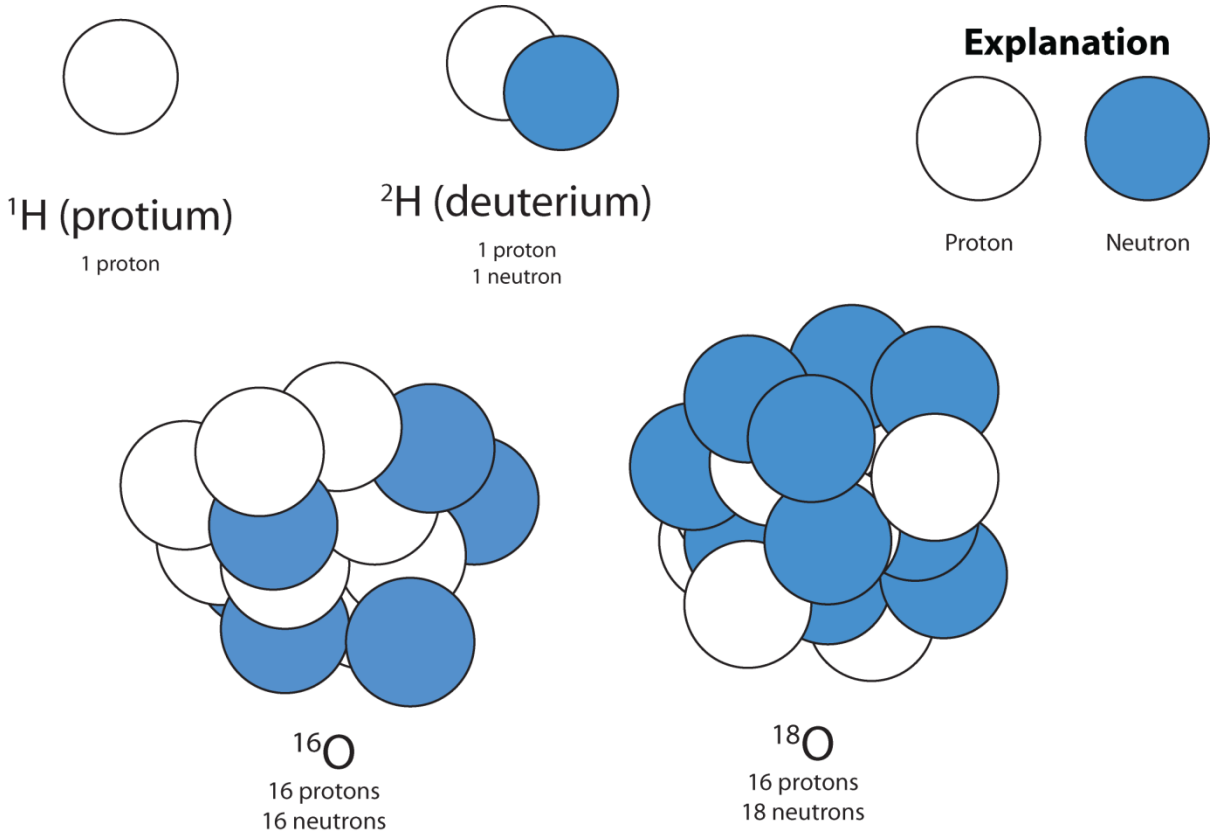

Figure 2.7: Schematic of a Bohr modelled nucleus for the stable isotopes of hydrogen (protium and deuterium) and oxygen (oxygen-16 and oxygen-18)

2.4.2. Abundance of Water Isotopologues

Isotopologues are molecules with the same elemental compositions, but with differing isotopic compositions. For example, water is composed of two hydrogen atoms and one oxygen atom. One isotopologue of water could be represented as two protium atoms and one oxygen-16 atom. A second isotopologue could be represented by two protium atoms, but bonded to an oxygen-18 atom. These compositions are both water molecules, but different with respect to their isotopic composition. As there are 2 isotopes of hydrogen and 3 isotopes of oxygen, a total of nine possible combinations, or isotopologues, exist for water molecules (Kendall and Coplen, 2001; Sharp, 2007; Gat, 2010). The percent abundance of each atom, or isotope, and isotopolgues are presented in Table 2.2. Ultimately, the different isotope ratios

of water, or isotopologues, between hydrologic reservoirs in natural systems are the basis of tracing waters.

Stable Isotope	Average abudance (%)
H (protium)	99.9844
D (deuterium)	0.01557
^{16}O	99.7621
^{17}O	0.03790
^{18}O	0.20004
Isotopologue	**Average abundance (%)**
$H_2 16O$	99.73098
$H_2{}^{18}O$	0.199978
$H_2{}^{17}O$	0.031460
$HD^{16}O$	0.0000006
$HD^{18}O$	0.0000001
$D_2{}^{16}O$	0.00000002
$D_2{}^{17}O$	0.0000000001
$D_2{}^{18}O$	0.0000000005

Table 2.2: Relative abudance of water isotope species and isotopogues of water (modified from Sharp, 2007)

2.4.3. Water Isotope Ratios and Standards

Stable isotopic compositions are represented as a relative differences in units of parts per thousand (per mille deviation) as the absolute isotopic compositions cannot be defined easily with high levels of precision (McKinney et al., 1950). Relative differences in isotopic compositions are denoted by the Greek lowercase symbol delta (δ) and measured against an international reference-scale, which for water isotopes is the isotopic composition of Vienna Standard Mean Ocean Water, or VSMOW (Equation 2.4) (Araguás-Araguás et al., 2000; Clark and Fritz, 1997).

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000 \text{ ‰ VSMOW} \qquad \text{Equation 2.4}$$

R is the ratio of heavier to lighter isotopes; R_{sample} is the ratio of the sample; $R_{standard}$ is the abbreviation for the referenced standard.

The original international reference-scale for water isotopes was Standard Mean Ocean Water or SMOW (Craig, 1961b). However, SMOW from Craig (1961) did not actually exist. The reference value for SMOW was calibrated with respect to a sample from the Potomac River supplied by the Natural Bureau of Standards (Clark and Fritz, 1997). Subsequently, the International Atomic Energy Agency (IAEA) developed a distilled seawater sample aptly named Vienna SMOW (VSMOW). VSMOW is the current internationally accepted reference point for water isotope ratios (HAGEMANN et al., 1970; Baertschi, 1976; Clark and Fritz, 1997). Gonfiantini (1978) developed the Standard Light Antarctic Precipitation (SLAP) reference, which provides a lower bounding point for water isotope compositions. These two standards (VSMOW and SLAP) allow for a two-point calibration of measured water isotope ratios.

2.4.4. Global Meteoric Water Line

Like the hydrological cycle, isotope hydrology begins with the ocean. Logically, the reference standard VSMOW is equal to 0 ‰ for both δD and $\delta^{18}O$. Friedman (1953) first observed that for δD and $\delta^{18}O$ values of natural waters, a strong positive covariance exists between δD and $\delta^{18}O$. These observations were based on hydrogen isotope analyses Friedman had conducted and later combined with $\delta^{18}O$ data from Epstein & Mayeda (1953). From a large global compilation of freshwaters, Craig (1961) showed that:

$$\delta D = 8\delta^{18}O + 10 \qquad \text{Equation 2.5}$$

This equation defines the Global Meteoric Water Line (GMWL) (Figure 2.8). However, from Figure 2.8, it can be seen that the GMWL does not pass through the value associated with its ocean origin where:

$$\delta D = 0;\ \delta^{18}O = 0 \qquad \text{Equation 2.6}$$

The separation of the GMWL from SMOW results from the kinetic fractionation effects associated with the evaporation of ocean water as the air above the ocean and liquid water in the oceans are not in isotopic equilibrium resulting in a deuterium excess (i.e. δD = + 10‰) (Sharp, 2007). Globally, the average relatively humidity is approximately 85%. Likewise, precipitation from water vapour having formed with a relative humidity of 85% has a

deuterium excess of +10‰. Accordingly, the deuterium excess for global precipitation should therefore have an average of +10‰, which it does, as evidenced by the positioning of the GMWL.

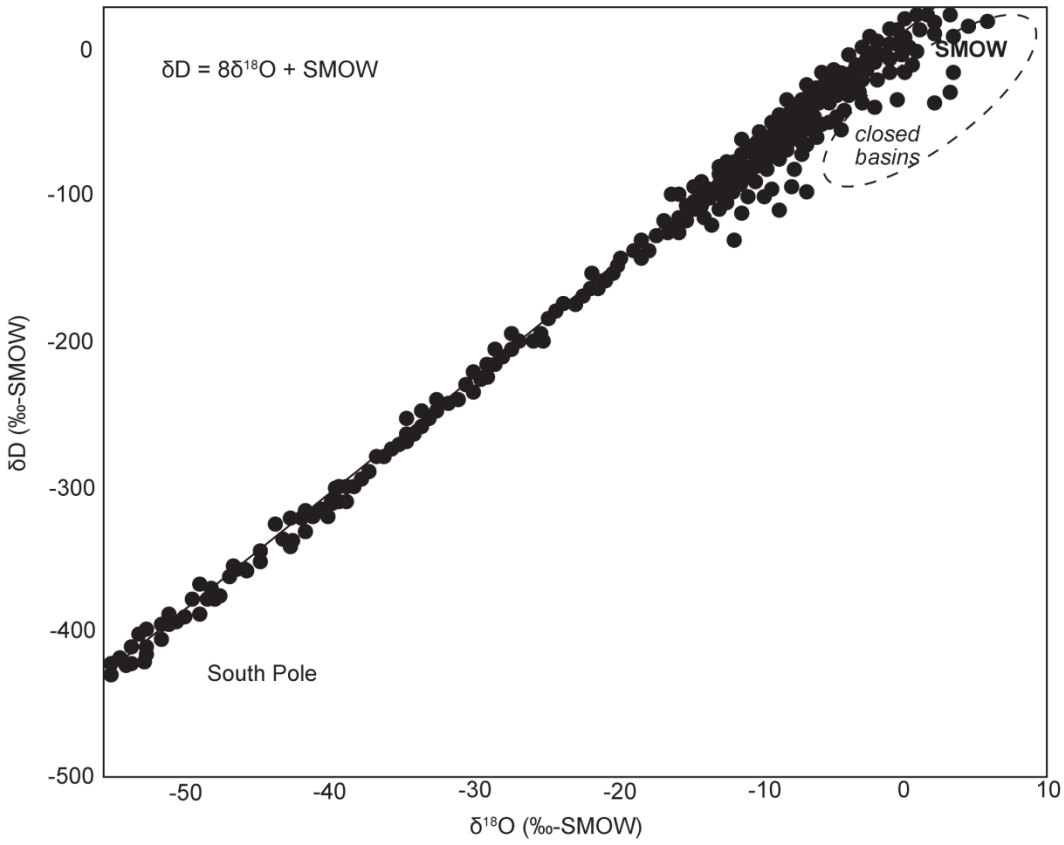

Figure 2.8: The global meteoric water line (GMWL) is defined by a global compilations of meteoric waters. Lower latitudes and colder regions generally plot in the more negative ranges (i.e. South Pole) while more tropical regions plot relatively in more positive ranges (modified from Sharp, 2007).

Deuterium excess, *d*, is represented by the positioning of δD relative to VSMOW for any given δD and $\delta^{18}O$ value (Equation 3.4). In other words, *d* is the y-intercept of given samples δD and $\delta^{18}O$ value assuming a slope = 8 and passing through VSMOW.

$$\delta D = 8\delta^{18}O + d \qquad \text{Equation 2.7}$$

Solving for *d* yields

$$d = \delta D - 8\delta^{18}O \qquad \text{Equation 2.8}$$

Dansgaard (1964) interprets *d* to be a representative value of non-equilibrium fractionation occurring during the original evaporation and condensation of water vapour that is associated with the collected precipitation. Deuterium-excess values can serve as an estimate and delineation of moisture sources to precipitation (Gat, 1996; Craig and Gordon, 1965), however it is stressed that multiple factors including the sources of air masses, temperature, aridity, relative humidity, and wind speed are all attributed to the *d* value and considering moisture origins (Sharp, 2007). These variables may change dramatically through time.

2.4.5. Controls on the Stable Isotopic Composition of Precipitation

Variance in the isotopic composition of water is associated with the cumulative effects of equilibrium, kinetic, and Rayleigh-distillation isotopic fractionation. Equilibrium fractionation is characterized by equal forward and backward exchange rates, however this does not predicate similar isotopic compositions, but rather different isotope ratios between compounds (Kendall and Caldwell, 1998). As an example, equilibrium fractionation occurs during the condensation of water vapour to water droplets. Heavier isotopes thermodynamically 'prefer' lower energy states and thus ^{2}H and ^{18}O preferentially go into the liquid phase rather than staying in the gaseous phase. Thus, the liquid phase is said to be enriched in ^{2}H and ^{18}O while the vapour phase is depleted in ^{2}H and ^{18}O.

Unlike the 'closed system' of equilibrium fractionations, kinetic fractionation is characterized by non-reversible reactions in an 'open system'. An example of this is the evaporation of water. Notably, equilibrium fractionation does take place in evaporation whereby there is an equal exchange between liquid water and water vapour at the air-water interface. However, in the presence of external factors over the ocean (i.e. wind), isotopically depleted water vapour is removed from air-water interface (the 'closed' system) and subsequently to the atmosphere. The removal of isotopically depleted water vapour defines evaporation as being out of isotopic equilibrium and therefore a kinetic fractionation (Clark and Fritz, 1997). The net result is such that, globally, the ocean is enriched in ^{2}H and ^{18}O while water vapour over the oceans is relatively depleted in ^{2}H and ^{18}O.

Rayleigh fractionation, or distillation, involves the progressive depletion of ^{2}H and ^{18}O from air masses. ^{2}H and ^{18}O is progressively removed from parent air masses by subsequent precipitation. Two global-scale examples of Rayeligh fractionation are the transport and rainout of air masses across continents (also known as the continental effect) and progressive

rainout of air masses transported from equatorial regions poleward (latitude effect). A detailed description of Rayleigh fractionation is presented in Sharp (2007).

Seminal work by (Friedman, 1953; Merlivat and Jouzel, 1979; Rozanski et al., 1993; Gat, 1996; Dansgaard, 1964; Araguás-Araguás et al., 2000) have described several factors relevant to the interpretation of the isotopic composition of precipitation. These factors include the altitude, amount, continental, latitude, seasonality, and temperature effects. A summary of these isotope effects are presented in Appendix 1. Ultimately, the dominant factor in the isotopic composition of precipitation is related to the vapour fraction remaining in the originating air mass when precipitation occurs (i.e. Rayleigh fractionation). Notably, temperature is intrinsically related to the residual vapour fraction of water vapour and thus to the isotopic composition (Figure 2.9) (Sharp, 2007).

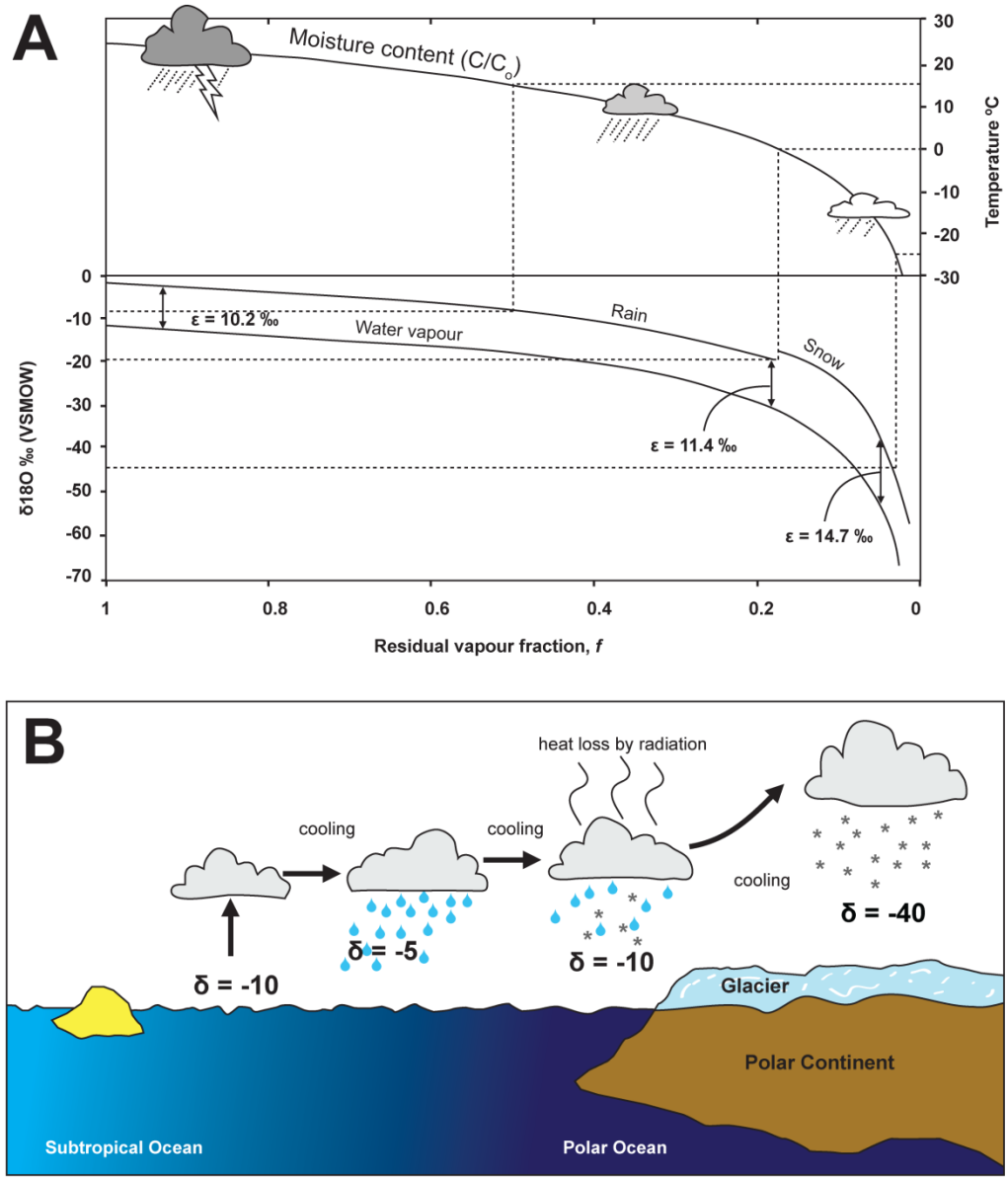

Figure 2.9: A) An example of Rayleigh distillation where ^{18}O values become more negative with subsequent rainout and decreasing temperature. With decreasing temperature, air masses hold less moisture, thus the relationship with residual vapour fraction. B) Example of Rayleigh distillation through the poleward transport of moisture from equatorial regions (modified from Clark & Fritz 1997; Allègre 2008).

2.4.6. Local Meteoric Water Lines

The GMWL represents a best-fit line through precipitation on a global scale, however, the GMWL may not accurately represent MWLs at local to regional scales. From combined climatic and geographic effects, these factors give rise to local meteoric water lines (LMWLs). LMWLs may not always deviate strongly from the GMWL. However, some general inferences can be made based on their position relative to the GMWL (Figure 2.10).

For example, based on the premise of defining LMWLs with respect to origin, Weyhenmeyer (2002) developed two LMWLs for precipitation (northern and southern moisture sources) falling on the Batinah Coastal Plain in Oman and plotted subsequent groundwater isotopic compositions with these LMWLs. Their findings show that groundwater in this system likely to be a mixture of precipitation derived from these two distinct sources.

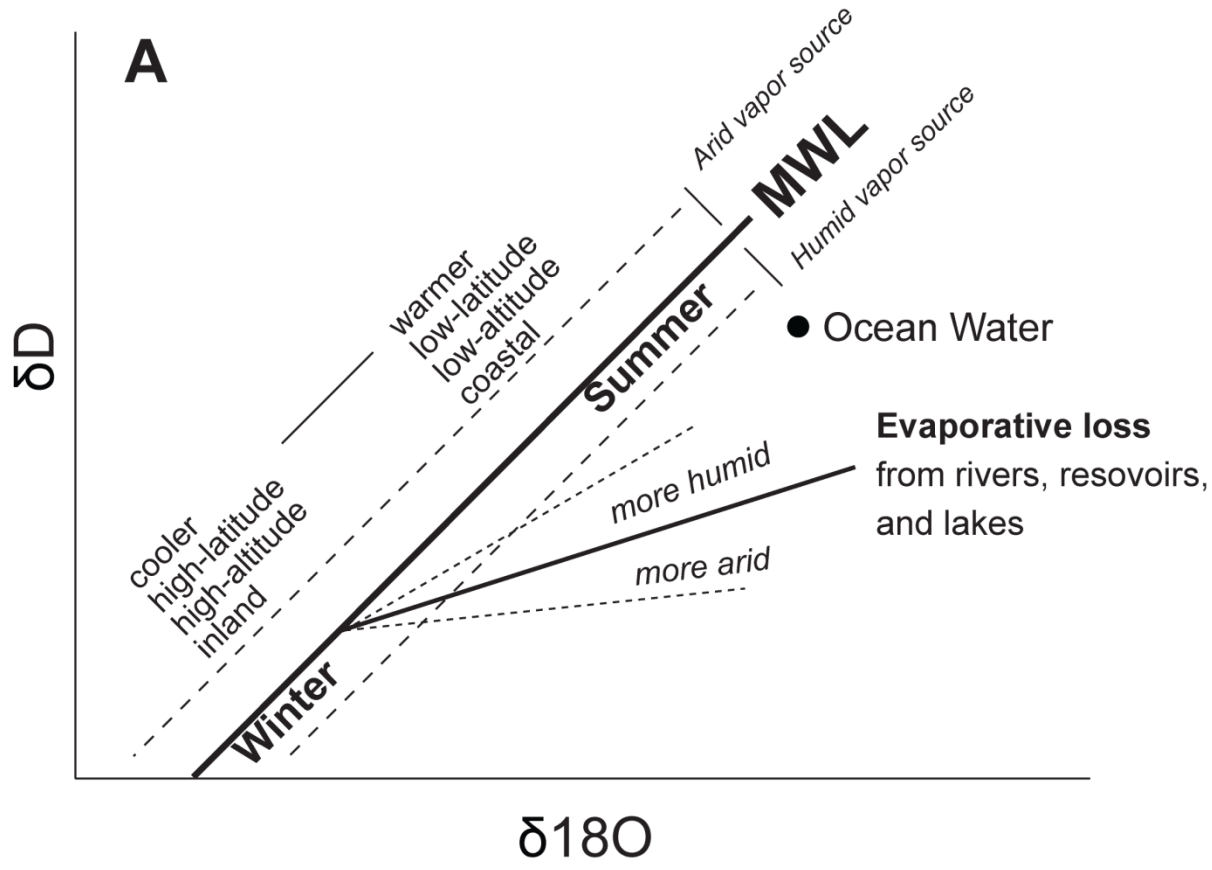

Figure 2.10: Possible climatological interpretations based on relative positions of δD and δ18O data in a bivariant plot (SAHRA, 2005)

2.4.7. Line-Conditioned Excess Method

LMWLs, however, are not solely qualitative. Landwehr & Coplen (2004) present a new method to assess the co-variance between δ^2H and δ^{18}O ratios of river samples to a derived LMWL or the GMWL they describe as a line-conditioned excess ($LMWL_{excess}$ for a LMWL or $GMWL_{excess}$ if comparing to the GMWL). Although similar to the concept of *d*, a line-conditioned excess is defined as

$$LMWL_{excess} = \delta\ ^2\mathrm{H} - a\delta^{18}\mathrm{O} - b \qquad \text{Equation 2.9}$$

Where *a* (slope) and *b* (y-intercept) are the coefficients present in an observed MWL. For the $GMWL_{excess}$, the values of *a* and *b* are correspondingly 8 and 10, respectively (Equation 2.10).

$$GMWL_{excess} = \delta\ ^2H - 8\delta^{18}O - 10 \qquad \text{Equation 2.10}$$

For example, a δD and $\delta^{18}O$ value that plotted close to a particular LMWL would have a $LMWL_{excess}$ close to that of 0‰. Another example would be a δD and $\delta^{18}O$ value that plotted close the GMWL would have a *d* value of +10‰, but its $GMWL_{excess}$ would be close to 0 ‰ as there is minimal deviation from the GMWL.

Furthermore, a one standard deviation of uncertainty, *S*, based on analytical errors can be defined for any MWL as

$$S_{MWL} = \left\{(\text{analytical error of } {}^2H)^2 + \left(a(\text{analytical error of } \delta^{18}O)\right)^2\right\}^{0.5} \qquad \text{Equation 2.11}$$

S_{MWL} may then be used to assess significant departures from a LMWL and the GMWL as

$$MWL_S = \frac{[\delta\ ^2H - a\delta^{18}O - b]}{S} \qquad \text{Equation 2.12}$$

or as applied to the GMWL

$$GMWL_S = \frac{[\delta\ ^2H - 8\delta^{18}O - 10]}{S} \qquad \text{Equation 2.13}$$

Theoretically, cumulative precipitation, surface, and groundwater may also be compared against MWLs using line-conditioned excesses.

An example of this could be where the LMWL for a hypothetical Location X (LMWL-X) is observed to be

$$\delta D = 7\delta^{18}O + 8 \qquad \text{Equation 2.14}$$

The $LMWL_{excess}$ for LMWL-X would therefore be written as:

$$X_{excess} = \delta\ ^2H - 7\delta^{18}O - 8 \qquad \text{Equation 2.15}$$

For the calculation of *S* for location X, the analytical errors of the University of Canterbury Stable Isotope Facility are 1‰ and 0.2‰ for δD and δ18O, respectively. This yields a value

of S equal to 1.7. Therefore, the standard deviation of any δD and $\delta^{18}O$ value from the LMWL-X may then be represented as:

$$LMWLX_S = \frac{[\delta\ ^2\mathrm{H} - 7\delta^{18}\mathrm{O} - 8]}{1.7} \qquad \text{Equation 2.16}$$

This provides a statistically robust method for which δD and $\delta^{18}O$ values of subsequent datasets (i.e. cumulative precipitation, surface waters, and groundwater) may be directly compared against MWLs.

2.4.8. Importance of Characterizing Isotopic Variability Local Meteoric Waters

Characterizing the local variations in the isotopic composition of precipitation are important as they are used to assess possible kinetic effects (*d* and line-conditioned excess) not only for moisture source analysis, but also in defining end-member isotopic compositions of precipitation, which are essential parameters in stable isotope mixing models. Furthermore, these characterizations of meteoric waters are essential in creating mappable distributions of stable isotopes in precipitation that are globally significant.

2.5. Isoscapes

The term 'isoscape' is simply a compound word for "isotopic landscapes". Advances in both geographic information systems (GIS) and geostatistical analysis have facilitated the development of predictive models of spatial variability in isotopic compositions for a variety of applications (Bowen and Wilkinson, 2002; van der Veer et al., 2009; Bowen, 2010). Early interpolations of stable isotope distributions in precipitation were primarily based on more simple interpolation functions (kriging, inverse-distance weighted, etc.). Newer models are now able to account for both Rayleigh-type distillations (latitude and elevation effects) in addition to temperature and precipitation data (Figure 2.11). For sites where no collection for isotopes in precipitation has occurred, these models have significant predictive power with respect to both δD and $\delta^{18}O$ (Bowen and Revenaugh, 2003). Combinations of empirically derived functions from geostatisical analysis and Rayleigh-type assumptions in modelling both distributions and discrete point models of isotopic composition establish a powerful framework in which to trace water throughout the hydrosphere.

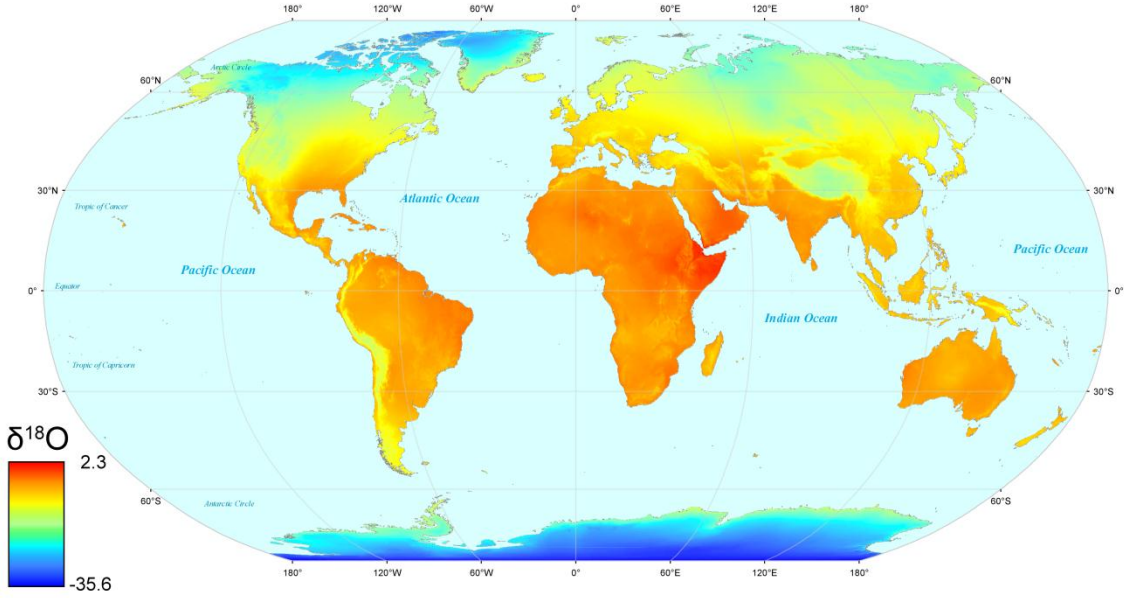

Figure 2.11: Isoscape of modern mean annual $\delta^{18}O$ (generated from data from Bowen & Revenaugh 2003)

2.6. Stable Isotopes in Hydrogeology

Based on the characterization of meteoric waters both on short and long-term scales (e.g. isoscapes), stable isotopes provide an alternative approach to purely physical characterizations of groundwater systems. Isotopic tracers provide ways to determine both groundwater origins and flowpaths, in areas where physical models can be limited (Weyhenmeyer, 2002; Criss and Davisson, 1996).

In the absence of high-temperature water-rock interactions, water isotopes are mass-conservative as they move through groundwater systems. Based on this principle, waters of different origin, or source, mix conservatively in groundwater systems. This principle allows for the quantification of relative contributions based on end-member modelling (Phillips & Gregg 2001). For example, if we consider a two-end member single species (a stable isotope in this case) mixing model. Where *Q* equals the inflow volume and *x* equals the concentration of a solute species

$$Q_1 x_1 + Q_2 x_2 = Q_p x_p \qquad \text{Equation 2.17}$$

$$Q_1 + Q_2 = Q_p \qquad \text{Equation 2.18}$$

Dividing by Equation 3.11 yields

$$\delta_{p1}x_1 + \delta_{p2}x_2 = y_p \qquad \text{Equation 2.19}$$

$$\delta_{p1} + \delta_{p2} = 1 \qquad \text{Equation 2.20}$$

We can therefore solve for either fraction of the end-members. For example solving for the fraction of 'p1' equals

$$\int_{p1} = \frac{\delta_M - \delta_{p1}}{\delta_{p1} - \delta_{p2}} \qquad \text{Equation 2.21}$$

Moreover, assuming 'M', 'p1', and 'p2' are measured independently, a first-order Taylor series approximation of variance for can be calculated using partial derivatives (Taylor, 1982) as

$$\sigma^2_{\int_{p1}} = \left(\frac{\delta \int_{p1}}{\partial \delta_M}\right)^2 \sigma^2_{\delta_M} + \left(\frac{\delta \int_{p1}}{\partial \delta_{p1}}\right)^2 \sigma^2_{\delta_{p1}} + \left(\frac{\delta \int_{p1}}{\partial \delta_{p2}}\right)^2 \sigma^2_{\delta_{p2}} \qquad \text{Equation 2.22}$$

Equation 3.15 reduces to

$$\sigma^2_{\int_{p1}} = \frac{1}{(\delta_{p1} - \delta_{p2})^2}\left[\sigma^2_{\delta_M} + \int^2_{p1}\sigma^2_{\delta_{p1}} + (1 - \int_{p1})^2 \sigma^2_{\delta_{p2}}\right] \qquad \text{Equation 2.23}$$

2.7. Summary

Mathematical constructions, such as the physical continuity equation, allow hydrologists to quantify and predict inflows and outflows between hydrological reservoirs. In particular, this thesis is focused with quantifying the fluxes from precipitation to surface and groundwaters of the CGS by using both physical and chemical analysis. The development of stable isotopic hydrological tracers has allowed for an unprecedented understanding of hydrologic fluxes in local water cycles that are not readily apparent from purely based physical characterizations. Such datasets also provide crucial insights into global scale phenomena such as the poleward transport of moisture and Rayleigh-type isotopic fractionation of air masses (e.g. the GMWL). At the regional to local scale, understanding the factors affecting the isotopic composition of precipitation allows researchers to use LMWLs as indicators of moisture origin and prior moisture transport processes across a variety of spatial scales. Through both GIS and geostatistical analysis, predictive models provide stable isotopic compositions, or isoscapes, for regions where little data may exist. These principles provide a theoretical framework and geochemical tool-set for the application of stable isotopes to hydrogeological systems. Given their conservative nature in groundwater systems, stable isotopes provide a

simple method of determining relative contributions from recharge sources and a way to independently test purely based physical hydrogeological models.

Chapter 3 : Study Area

3.1. Introduction

The Central Canterbury Plains represent the area of the larger Canterbury Plains located between the Waimakariri and Rakaia Rivers, eastern South Island, New Zealand (Figure 3.1). The Central Canterbury Plains are bound to the east by the Southern Pacific Ocean and the Southern Alps to the west. This study focused on the Christchurch Groundwater System (CGS) located in the eastern margin of the Central Canterbury Plains.

This chapter presents a review of the regional geologic setting, focusing on the the sedimentary framework and depositional history of the east coast, South Island, followed by a review of the geology and hydrogeology of the Central Canterbury Plains and the CGS. The chapter concludes with an overview of the climatic conditions of the South Island and the CGS study area.

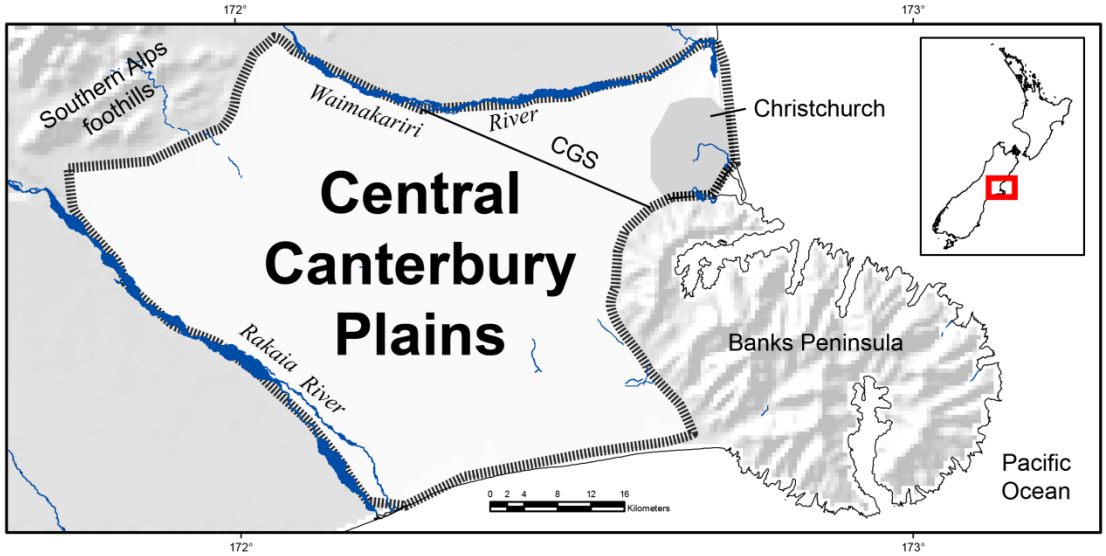

Figure 3.1: The Central Canterbury Plains are located between the Rakaia and Waimakariri Rivers

3.2. Geology

3.2.1. Regional Geologic Setting

The Southern Alps in New Zealand result from oblique convergence between the Indo-Australian and Pacific Plates, manifested as the Alpine Fault (Figure 3.2) (Adams, 1980; Koons, 1989; Koons, 1990). New Zealand's largest alluvial sequence, the Canterbury Plains, comprises approximately 8,000 km^2, which is as much as 70 km wide and 185 km long

(Leckie, 2003). The Canterbury Plains are primarily composed of the glacio-fluvial outwash delivered by braided alpine rivers originating in the Southern Alps. These sequences are composed of gravelly layers interceded, in places, by sand to silt sized fractions deposited during changes in the braided rivers sediment transport (Brown and Weeber, 1992; Leckie, 2003). Bedrock is dominated by the Torelesse Supergroup greywacke (Brown, 2001). The basement structure is a complex geosyncline delineated by ridges and troughs (Hicks, 1989). In places; alluvial deposits are interpreted to be up to 2,500 meters in depth and intruded by Banks Peninsula Volcanics on the eastern portion of the study area (Brown and Weeber, 1994; Hicks, 1989).

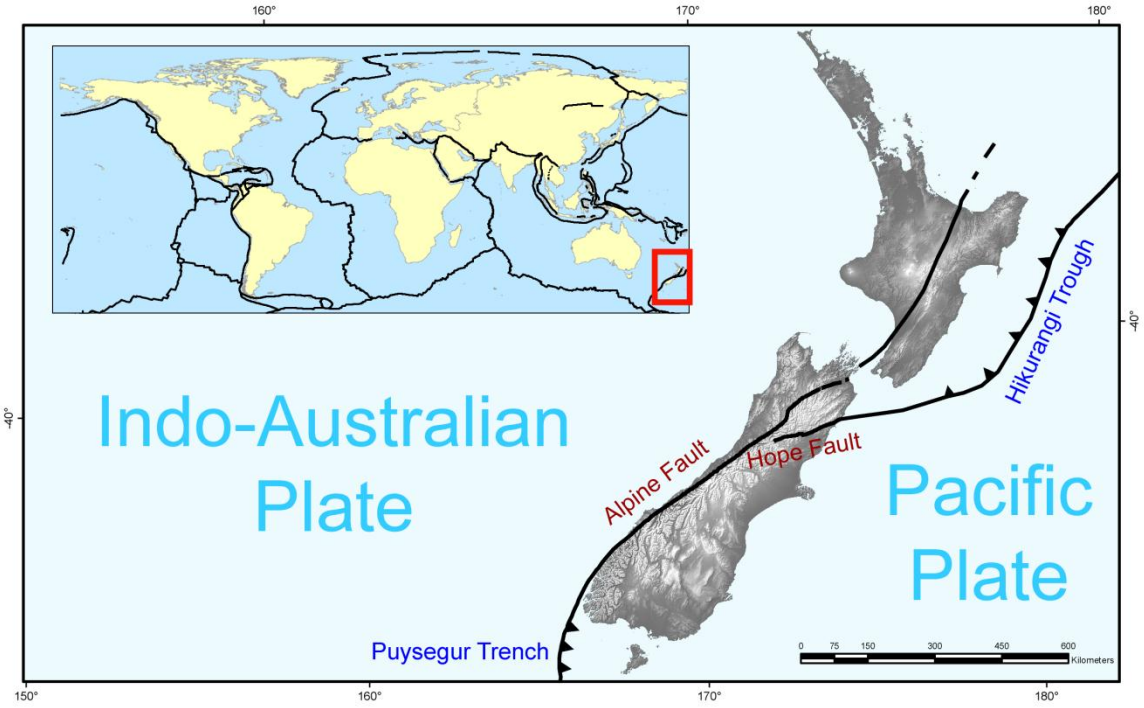

Figure 3.2: Tectonic setting of New Zealand

3.2.2. Geology of the Central Canterbury Plains

Extending from the Waimakariri River to the north and the Rakaia River to the south, the Central Canterbury Plains alluvial sequence is primarily composed of glaciofluvial deposits derived from the two rivers with approximately two thirds being derived from the Waimakariri (Figure 3.3) (Taylor et al., 1989; Brown, 2001). Inland, correlation between distinguishable and continuous sedimentary sequences is difficult as marker beds are difficult to identify (Weir, 2007; White, 2009). Towards the coast, distinguishable alternating sequences of interglacial marine sediments and dominantly glacio-fluvial outwash derived gravels are observed to approximately 240 meters depth (Wilson, 1976; Brown and Weeber,

1992). These alternating marine and gravel sequences make up the primary hydrogeologic framework of the CGS located in the eastern portion of the study area. More alluvial sediments are present with depth to bedrock, but their stratigraphy and depositional history are poorly understood. Banks Peninsula, on the south-eastern margin of the study area, is a highly eroded late Miocene age intra-plate shield volcanic complex consisting primarily of basaltic and trachytic deposits.

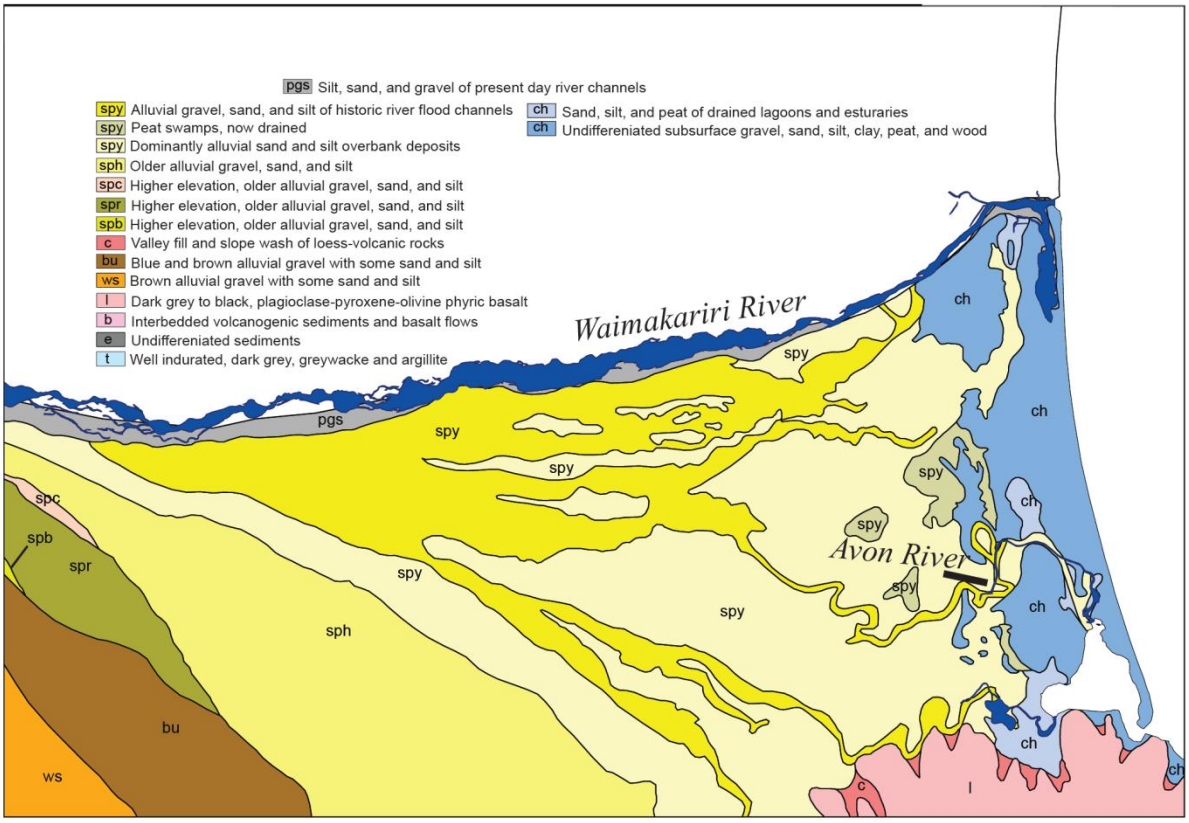

Figure 3.3: Surficial geology of the CGS (Brown and Weeber, 1992)

The Kaikoura Orogeny (Middle Tertiary to Early Quaternary), led to rapid uplift and erosion fuelling the deposition of significant volumes of fluvial outwash gravels along the eastern margin of the South Island New Zealand (Wilson, 1973; Wilson, 1976; Talbot et al., 1986). During periods of Quaternary glacial advances (i.e. Riccarton Gravel) increased glacio-fluvial outwash resulted in deposition of predominantly gravel. During glacial retreats when sea-levels were higher, near-shore and shallow marine deposits formed, and are inferred to represent beach, swamp, and near-shore environments (Wilson, 1973).

3.3. Hydrogeology

3.3.1. Christchurch Groundwater System

The CGS is characterized in the eastern portion by highly permeable gravel sequences interfingered by less permeable interglacial marine sediments. Artesian pressures are developed as water bearing sediments in the western portions of the CGS transition from unconfined, to semi-confined, and confined hydrologic conditions towards the coast (Figure 3.4). Permeable units in the sequences are duly called the Christchurch Artesian Aquifers. However, excluding the top confining layer within the CGS the overall hydrogeologic significance of the less permeable aquitards at depth in the CGS is debated as despite significant sedimentary heteorgeneity, locally, regional groundwater flow patterns are apparent (Hanson and Abraham, 2009). Higher transmisitivies are observed towards the coast where the larger continuous outwash gravel sequences occur appearing as 5-10 km wide corridors (Bal, 1996). For the purpose of this study, aquifers are delineated using the classification scheme of Weir's (2007) Canterbury Groundwater Model 2 (Table 3.1). Subsequent analyses of physical and chemical data in this thesis are therefore observed between different aquifers, which are relevant to potential changes in groundwater flow paths and chemistry that may change with depth.

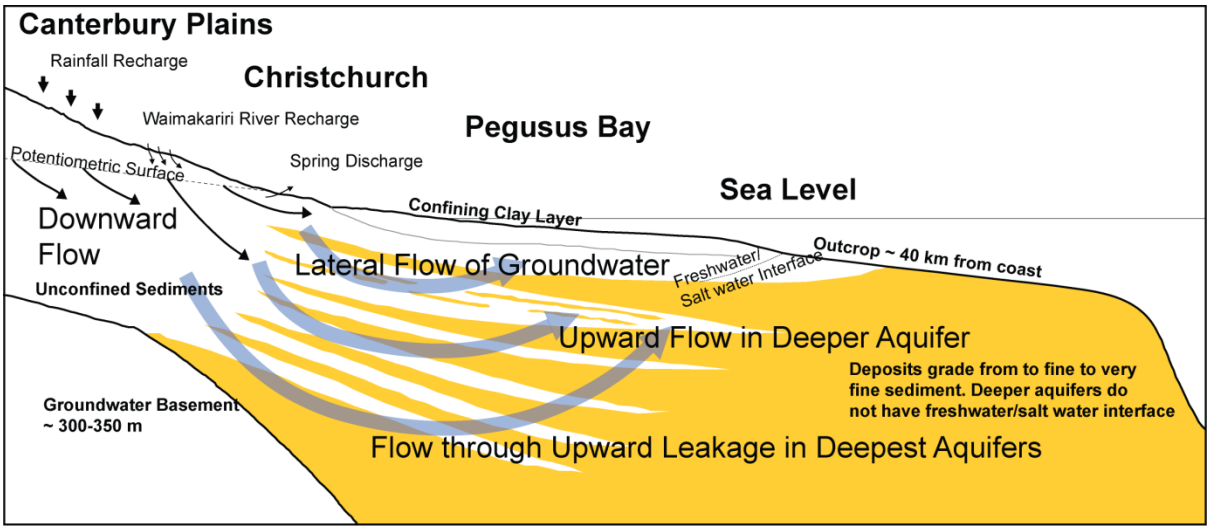

Figure 3.4: Schematic of recharge sources and groundwater flow paths in a generalized cross-section of the Christchurch Groundwater System (Talbot et al., 1986)

		Ranges in Depth (metres below ground level)	
Hydrogeological Layer	**Aquifer**	**Coastal**	**Inland**
1	Aquifer 1	0-30	0-40
3	Aquifer 2	30-80	40-110
5	Aquifer 3	80-130	110-140
7	Aquifer 4	130-190	140-200
9	Aquifer 5	>190	>200

Table 3.1: Aqualinc aquifer classification for the Central Canterbury Plains

3.3.2. The Avon River springs

Within the CGS, the Avon River originates from a network of depression springs occurring at the boundary of the confining layer at the approximate western boundary of the CGS (Figure 3.4) (White, 2009). The catchment of the Avon River springs, is defined by White (2009) using geological "pseudo-logs" and interpreted groundwater flowpaths. The Avon River springs catchment consists of an area generally north-northwest of the springs heads near the University of Canterbury with the northern boundary being the Waimakariri River. Previous studies suggest that the water recharging the Avon River springs is from the Waimakariri River recharge and subsequent declines in groundwater levels since European settlement have caused a downstream migration of spring heads (Wilson, 1976; Taylor et al., 1989; White, 2009).

3.3.3. Recharge Sources

Potential recharge sources for the CGS are considered to originate from rainfall infiltration and channel leakage from the Waimakariri River north of Christchurch (Haast, 1879; Haast, 2222; Hilgendorf, 1926; Woudt and Nicolle, 1978; Woudt et al., 1979; Hayward, 2002; Wilson, 1976; Taylor et al., 1989; Weir, 2007; Talbot et al., 1986). The relative contributions of these sources may vary significantly (Bidwell, 2005; Brown, 2001; Scott and Thorley, 2009). Estimates of channel leakage from simultaneous river gauging on the Waimakariri River range from 5 m^3/s to 14 m^3/s and with varying degrees of response to high-flows (Dalmer, 1971; Mandel, 1974; Cooper, 1980; White, 2009; Talbot et al., 1986). However, most groundwater models of the Canterbury Plains do not consider this full range and a constant recharge rate of 7 m^3/s (Talbot et al., 1986) is generally assumed (Di et al., 2005; Scott and Thorley, 2009). For the Canterbury Groundwater Model 2, Weir (2007)

incorporated variable losses from the Waimakariri River within the model structure and showed a similar average loss of 7 m^3/s. Moreover, the model also predicts losses from the groundwater system to the Waimakariri River. Furthermore, not all wells in the CGS respond to high river flows and only some wells show relatively steep hydraulic gradients (Woudt et al., 1979). It is important to consider then that ultimately, high river flows contribute to groundwater recharge and discharge via bank storage processes; however, this relationship does not appear to be linear (Mandel, 1974; Weir, 2007).

Estimates of rainfall infiltration are intrinsically related to soil types in the Canterbury Plains (White et al., 2003). Using observed infiltration rates (Hong, 2005) for discrete soil types in the Canterbury region, White (2009) estimates long-term recharge from rainfall within the Avon River springs catchment to be approximately 30 % of the annual rainfall amount, which broadly agrees with recharge estimates for the CGS from Scott (2004). However, spatial variations in rainfall infiltration rates inherently exist in the CGS, and are important in terms of larger regional water budgets (Scott, 2004).

3.3.4. Geochemistry of the Canterbury Plains Aquifers and the CGS

Central Canterbury Plains groundwaters, particularly those in the CGS, are predominantly bicarbonate type groundwater (Hayward, 2002). For any given area in CGS, the overall geochemistry is generally reflective of the predominant recharge source, whereby low ion and nutrient concentrations are representative of alpine recharge whereas rainfall recharge infiltration exhibits higher nutrient and ion concentrations (Burden, 1984; Hayward, 2002; Hanson and Abraham, 2009). Notably, the CGS does not follow classical models of increased ion concentrations with respect to depth in sedimentary basin aquifer systems (Chebotarev, 1955; Schoeller, 1959). Rather, with depth, maximum ranges in ion concentrations diminish in the CGS with only a small increase in median ranges likely due to the properties of the greywacke gravels (Hayward, 2002).

3.4. Climate

New Zealand lies in an area that encompasses the complex interaction between tropical anticyclones originating from the poleward side of the tropical Hadley Circulation and mid-latitude cyclones, making up the dominant westerly flow (Figure 3.5) (Sturman and Tapper, 1996; Sturman and Wanner, 2001). Air flow is further complicated by the presence of elongated axial mountain ranges (i.e. Southern Alps), that on the windward side give rise to annual rainfall amounts exceeding 10 000 mm and on the leeward side as little as < 400 mm

(Tomlinson, 1992; Lorrey et al., 2008). Conversely, the stark precipitation gradients also contribute to a significant difference in annual water deficits, particularly in the central and eastern portions of the South Island.

3.4.1. Climate of Christchurch

The CGS generally receives between 600-800 mm of rainfall annually with rainfall amounts increasing towards the coast and within the foothills of the Southern Alps and higher elevations on Banks Peninsula (Tomlinson, 1992). Air parcels and subsequent precipitation over the CGS study area may come from nearly any direction and temporally, are dynamic as large shifts in synoptic conditions can arise (Sturman, 2001). Rainfall is generally evenly distributed annually; however there is a slight autumn-winter maximum (Tomlinson, 1992). This is associated with increased southwesterly flow from the Southern Pacific Ocean during winter months coinciding also with increased moisture fluxes (i.e. contributing evaporation) over the 30º to 50º S latitudes (Sodemann and Stohl, 2009; Sturman and Tapper, 1996). Surface winds measured at the Christchurch International Airport during precipitation events show that the predominant wind direction during events is from the south (McGann, 1983). Moisture source modelling using back-trajectory analysis and stable isotope proxies, presented in subsequent chapter of this thesis, would greatly aid in understanding these uncertainties.

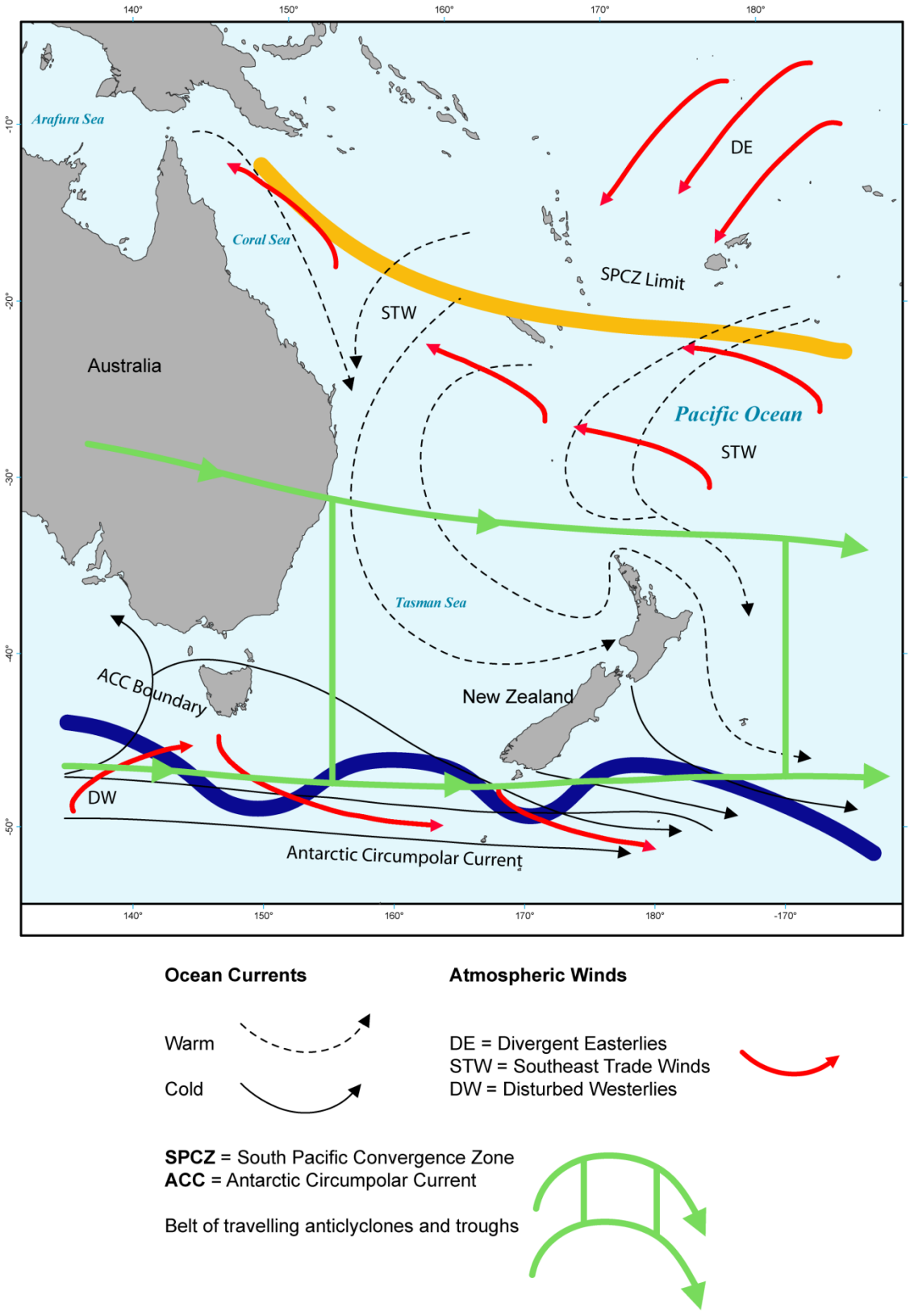

Figure 3.5: Regional climatic setting for New Zealand (Lorrey et al., 2008)

3.5. Summary

The South Island's dynamic landscape results from highly active and complex geological, hydrological, and climatological processes. The oblique convergence of the Pacific and Indo-Australian Plates gives rise to the Southern Alps. Subsequent erosion of the Southern Alps transported and deposited sediment, particularly in significant volumes during glacial advances, ultimately lead to the formation of the Canterbury Plains overlying above Torelesse bedrock. The Canterbury Plains are primarily composed of gravelly glacio-fluvial outwash, however during interglacial periods; higher sea-levels resulted in the deposition of marginal marine and shallow marine sediments. Hydrogeologically, the Canterbury Plains Groundwater System (< 200 meters depth) primarily consists of highly permeable water bearing gravels; however less permeable, lower yielding sediments are present and are associated with the interglacial high-stand finer grained sediments. Confining sediments towards the eastern margins of the study area give rise to artesian pressures in the CGS. Springs resulting from these pressures result in the Avon River springs surface water network. Recharge of this system has been proposed to be dominated by channel leakage from the Waimakariri River. Contributions are considered steady, however, some research suggests that high-flow events do contribute significantly. Rainfall is considered the other dominant recharge source; however its contribution is spatially and temporally variable. Despite the strong westerly flow present at this latitude globally, the long axial Southern Alps provide a major topographic barrier for which there are major differences in annual precipitation between the west coast and east coast, South Island. Christchurch's climate is highly variable and does not show strong seasonal variation. However, precipitation maximums do occur in the winter associated with increased southwesterly flow and moisture fluxes from the Southern Pacific Ocean.

Chapter 4 : Methodology

4.1. Introduction

In an effort to characterize meteoric, surface, and groundwaters of the CGS, 86 samples were collected from May 2009 to June 2010. In total, 61 precipitation events, 3 monthly cumulative rainfall collections, 13 springs, and 9 groundwater samples were collected and analysed for δD and $\delta^{18}O$ (Appendix 2). These data were complimented by previously published and unpublished data, facilitating interpretation of $\delta^{18}O$ variability within the CGS. Figure 4.1 indicates sampling locations of both primary and supplementary data used for this study. Unfortunately, recent earthquakes in Canterbury, New Zealand led to loss of several water samples, diminishing our original total to the reported number of samples above.

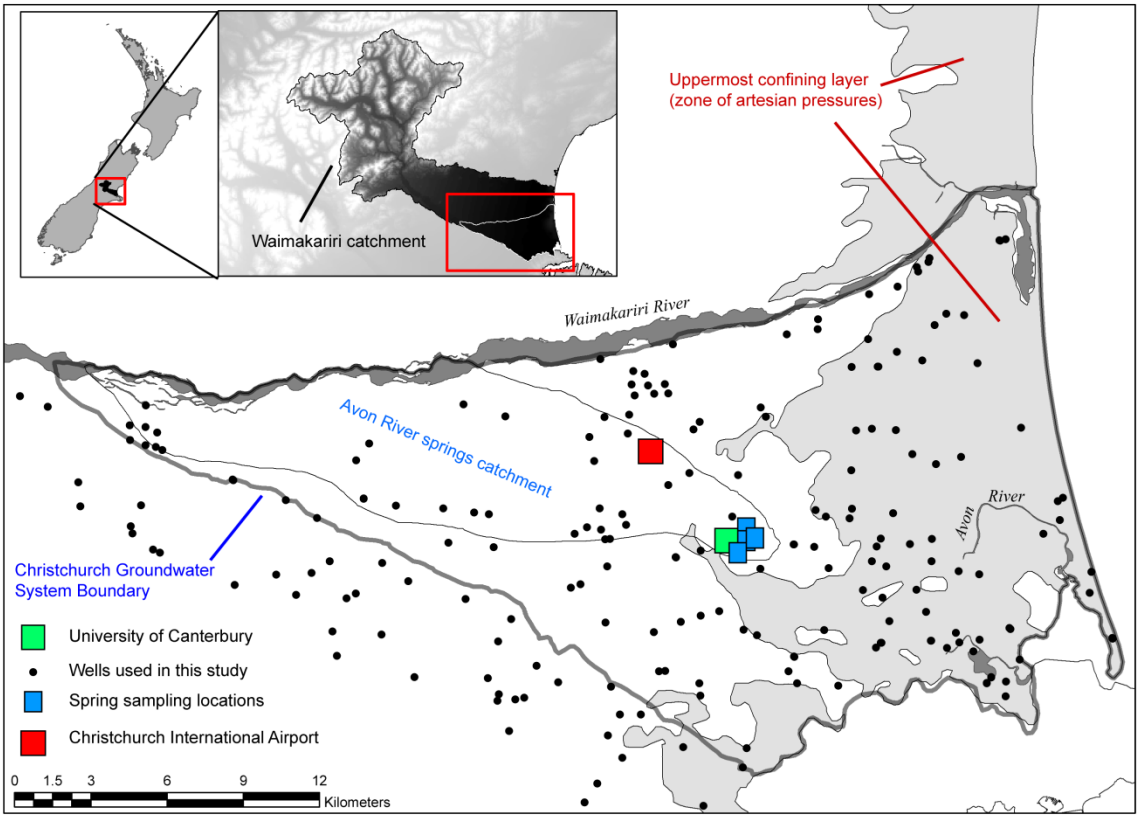

Figure 4.1: Study area map for the CGS, including wells and sampling locations for this study.

4.2. Field Investigations

All water samples were collected and stored in 20 and 30 mL glass vials. Precipitation event samples were collected using an 8 cm diameter funnel attached to a metal stand that funnelled

water into larger 20 to 100 mL plastic containers at the University of Canterbury campus. Surface water samples were collected as grab samples and also stored in 20 to 100 mL plastic containers (Koterba et al., 1995) . Groundwater samples were collected as part of quarterly Environment Canterbury groundwater sampling and collected according to their procedures (see Hanson & Abraham (2009). Upon collection, water samples were transferred from the plastic containers to glass vials and were stored in a refrigerator to protect against evaporation until stable isotope analyses were performed.

4.3. Stable Isotope Analysis

Stable isotope analyses of water samples were carried out at the University of Canterbury Stable Isotope Facility (UCSIF) using the UCSIF's Thermo Scientific TC/EA (Thermo-Combustion Elemental Analyser). Analyses were conducted using methods outlined in (Sharp et al. 2001) whereby samples are converted to $H_{2(g)}$ and $CO_{(g)}$ at 1400 ºC in a ultra-high purely helium stream. This mixed gas is then separated in to discrete phases by a 5 Aº mol sieve gas chromatography column. Sample gas was introduced to a Delta V Plus IRMS through a CONFLOIII split. δ-values were obtained from the integration of peaks recorded by the mass spectrometer and referenced to two IAEA standards (V-SMOW and SLAP) using a two-point calibration (Coplen, 1996). External analytical precision standard deviation is ±1 ‰ and ±0.2 ‰ for δD and $\delta^{18}O$, respectively.

4.4. Back-trajectory analysis

Air parcel moisture source determinations were performed using isentropic back-trajectories calculated from the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model. Back trajectories were run using the REANALYSIS global dataset. Particles were released for 72 hours from the University of Canterbury sampling location's latitudinal and longitudinal coordinates at the elevations of 500, 1500, and 2500 metres above sea level. These elevations were chosen as precipitation is likely to originate somewhere in this altitude range (Breitenbach et al., 2010). To assess the spatial variability of back-trajectories during the sampling period, a trajectory was calculated for each hourly interval. These results provide a robust spatial constraint on regional air parcel pathways across the time periods for which precipitation samples were collected. An example HYSPLIT analysis output showing multiple trajectories calculated for the sampling collection period from the three altitudes are presented in Figure 4.2. Results for all simulations are presented in Appendix 3.

Back-trajectory analysis was not carried for all of the precipitation samples. Of the 64 precipitation samples, 12 samples have been omitted. The reason for their exclusions was that either: no date can be resolved associated with the sample due to poor labelling; multiple samples were taken for the same time period with variation of stable isotope values within analytical error; or no precipitation was actually measured by local NIWA weather stations suggesting an inaccurate label of the collection date.

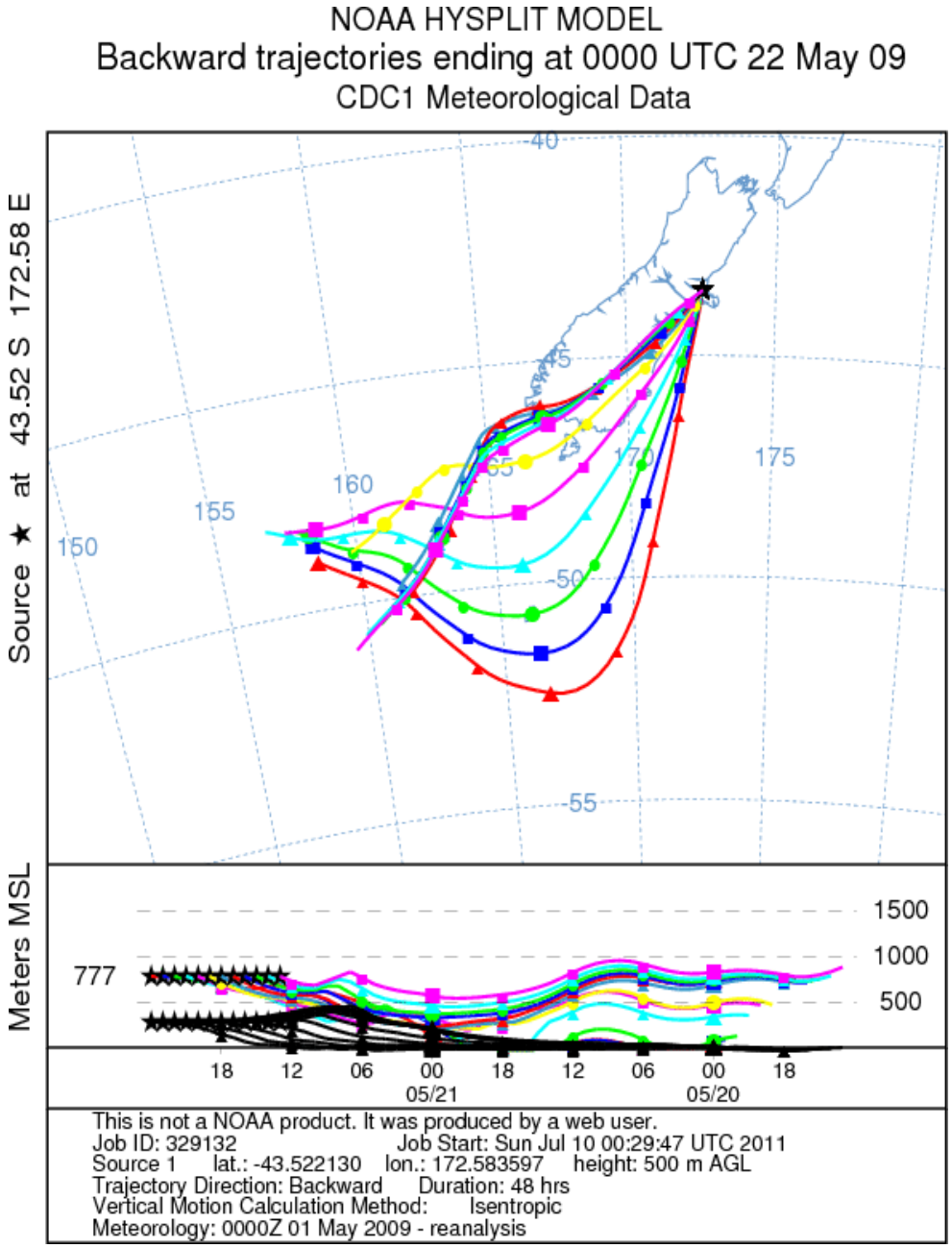

Figure 4.2: Example output from NOAA HYSPLIT back-trajectory simulation for 22 May 2009 event

4.5 Binary Mixing Model

The single element binary mixing model implemented in this study to calculate relative contributions of recharges sources to the Avon River springs is based on the method described in Phillips & Gregg (2001). The mixing model assumes that for the Avon River springs, an end-member composition, in this case a $\delta^{18}O$ value can be determined for each recharge source. Since groundwaters mix conservatively, the model can calculate the contributing fraction of an end-member for any given sample, or mixture, taken from the Avon River springs. Variability of end-member compositions are considered as sources of error, or uncertainty, and a standard error is presented alongside calculations of end-member contributions based on a Taylor Series approximation of variance (see Section 2.6.). Recent stable isotope applications, particularly in biogeochemistry, have stressed the need of reporting these errors associated with mixing models as the inherent variability in natural systems must be taken into account in mixing models (Phillips and Gregg, 2001b; Phillips and Koch, 2002; Parnell et al., 2010; Turner et al., 2010; Le Bot et al., 2011).

$\delta^{18}O$ values used in the model were compiled from numerous sources alongside original data collected for this thesis. The $\delta^{18}O$ values used for the Waimakariri River end-member predominantly came from the ECan Water Quality Database from 1978 to 1981, however the five samples collected for this thesis are included. $\delta^{18}O$ for cumulative precipitation was sourced from Taylor (1990). Lysimeter infiltration $\delta^{18}O$ values were taken from Stewart et al. (2002). Avon River springs δ-values were taken from data collected for this thesis. Spatial distributions of $\delta^{18}O$ are also presented for Aquifers 1 and 2 to accompany this. These datasets of $\delta^{18}O$ were obtained from the ECan Water Quality Database timestamped from January 2006 to 2010.

4.6 Potentiometric Surfaces

Previous interpolations of potentiometric surfaces include groundwater levels from multiple aquifers (Wilson, 1976; Stewart et al., 2002; Scott and Thorley, 2009). These potentiometric surfaces, however, would not accurately capture variability in hydraulic head with depth in the groundwater system. Therefore, a potentiometric surfaces was generated using ArcGIS software for Aquifer 4 showing the average groundwater level from 2006-2010. For the interpolation procedure, a simple 12-point spherical kriging method was used.

4.7. Summary

A suite of analytical methods were used in this study to characterize the isotopic variability of Christchurch precipitation, at multiple temporal scales, and its subsequent relationship to the surface- and groundwater systems of the CGS. A binary mixing model using $\delta^{18}O$ values for monthly precipitation, rainfall infiltration, and the Waimakariri River was developed to assess the relative contributions of the Waimakariri River to the Avon River springs. Furthermore, to characterize groundwater processes at depth, it is therefore critical to consider both the groundwater chemistry and groundwater flow for deeper aquifers. Most groundwater models for the CGS predict that groundwater from the Central Canterbury Plains flows southeast, and away from the CGS. This forms the basis of the CGS being managed as its own allocation zone.

Chapter 5 : Stable Isotopic Variability in Precipitation Events

5.1. Introduction

This chapter presents the stable isotopic of precipitation event samples collected at the University of Canterbury from May 2009 through July 2010. For each sample, $\delta^{18}O$, δD, and deuterium excess (*d*) were determined. Precipitation source regions associated for each precipitation sample are also presented. From these data, local meteoric water lines (LMWLs) are presented for each source origin, and possible relationships to climatological conditions at the time of precipitation are also discussed. A sub-set of these data are for tropical cyclone events sampled during May and June 2010.

5.2. δD, $\delta^{18}O$, and *d* Compositions of Precipitation Event Samples

Overall, the 65 Christchurch precipitation event samples exhibit a large range in isotopic composition (Figure 5.1). δD and $\delta^{18}O$ values range between -171.7 and 0.37, and -21.3 and -0.4 ‰, respectively. This range in values is comparable to continental-scale intra-annual variability (Bowen, 2008). The outlying δD and $\delta^{18}O$ value of -171.7, -21.3 ‰ was collected during a tropical cyclone and will be discussed in more detail in Section 5.4. Excluding this measurement, isotopic compositions ranged between 0.0 and -110.0 and 0.0 and -14.0‰ for δD and $\delta^{18}O$, respectively. Deuterium excess values calculated range between -15.0 and 24.0 ‰. A linear regression through the data shows a similar slope and slightly more negative y-intercept ($\delta D = 8.1\delta^{18}O) + 7$) compared to the GMWL ($\delta D = 8.0\delta^{18}O) + 10.0$). All δD, $\delta^{18}O$, and *d* are tabulated in Appendix 2.

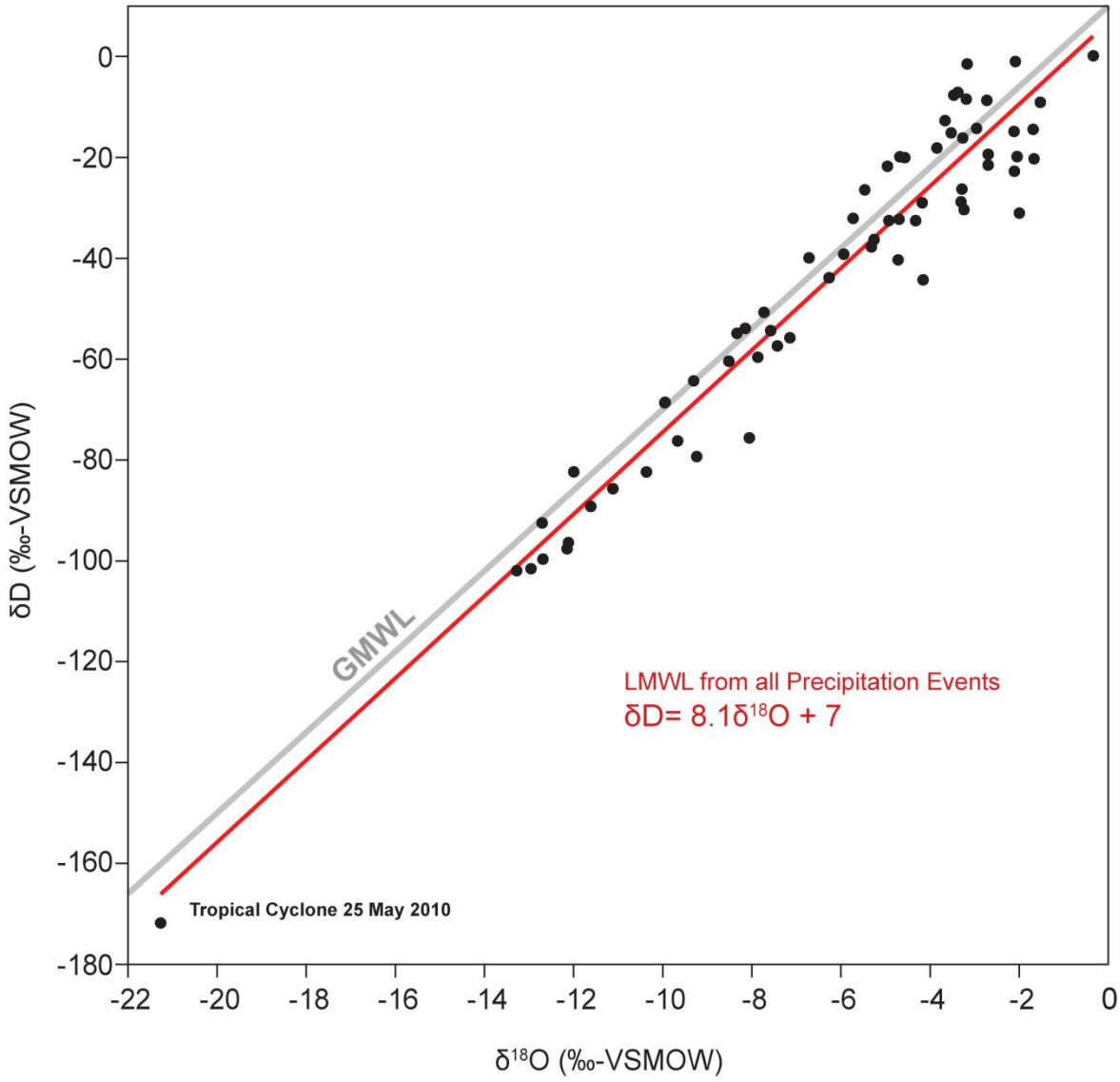

Figure 5.1: δD and $\delta^{18}O$ covariate plot for all precipitation events

5.3. Isotopic Variability between Moisture Sources

5.3.1. Back-trajectory analysis: defining regional areas of moisture origin

Back-trajectory analysis suggests that three general areas can be delineated from the air-parcel pathways analysed during the sampling period for precipitation falling over Christchurch. These paths originate in the Tasman Sea, the Tropical Pacific, and the Southern Pacific Ocean west, north, and south of the South Island (Figure 5.2). A total of 53 samples and their respective collection intervals were run using HYSPLIT. Seven of the HYSPLIT outputs, at this time, are inconclusive with respect to the moisture origins. Fourteen events were identified to originate from the Tropical Pacific Ocean. Thirteen samples were

identified to be sourced from the Tasman Sea. 19 samples were identified to originate from the Southern Pacific Ocean. For all of the precipitation event back-trajectory analyses results, these data are presented in Appendix 3.

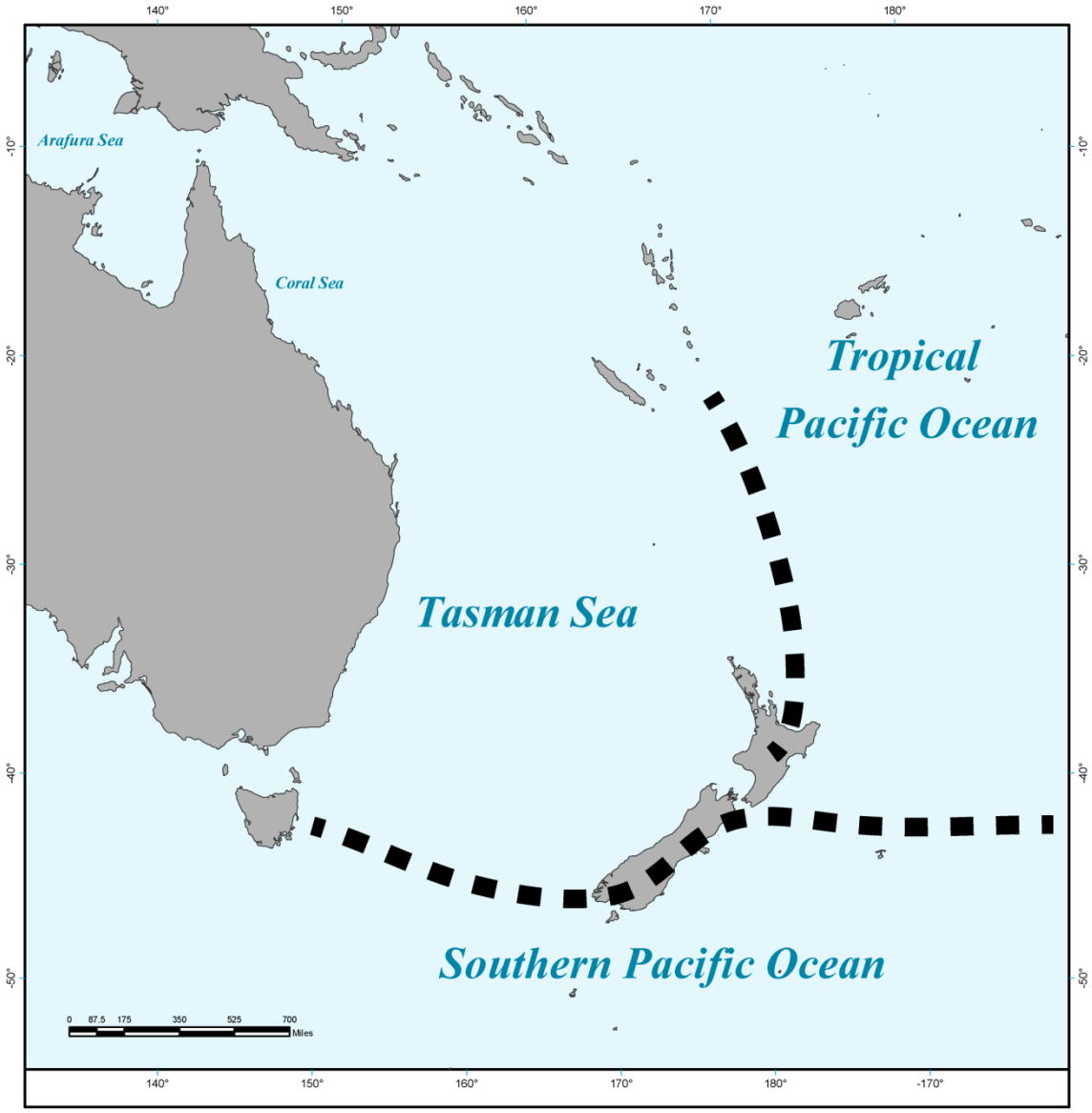

Figure 5.2: Generalized moisture source regions for Christchurch Precipitation

5.3.2. Isotopic Variability and Meteoric Water Lines of Similar Moisture Origin

Ranges in $\delta^{18}O$ values vary between interpreted moisture source regions (Figure 5.3). The Southern Pacific Ocean and the Tropical Pacific Ocean sample have very similar ranges; however the 25th, 75th, and median values for the Tropical Pacific Ocean are lower than Southern Pacific Ocean and the Tasman Sea. Similar medians are observed between the

Tasman Sea and the Southern Pacific Ocean, however more positive 25th and 75th quartiles are observed for the Tasman Sea.

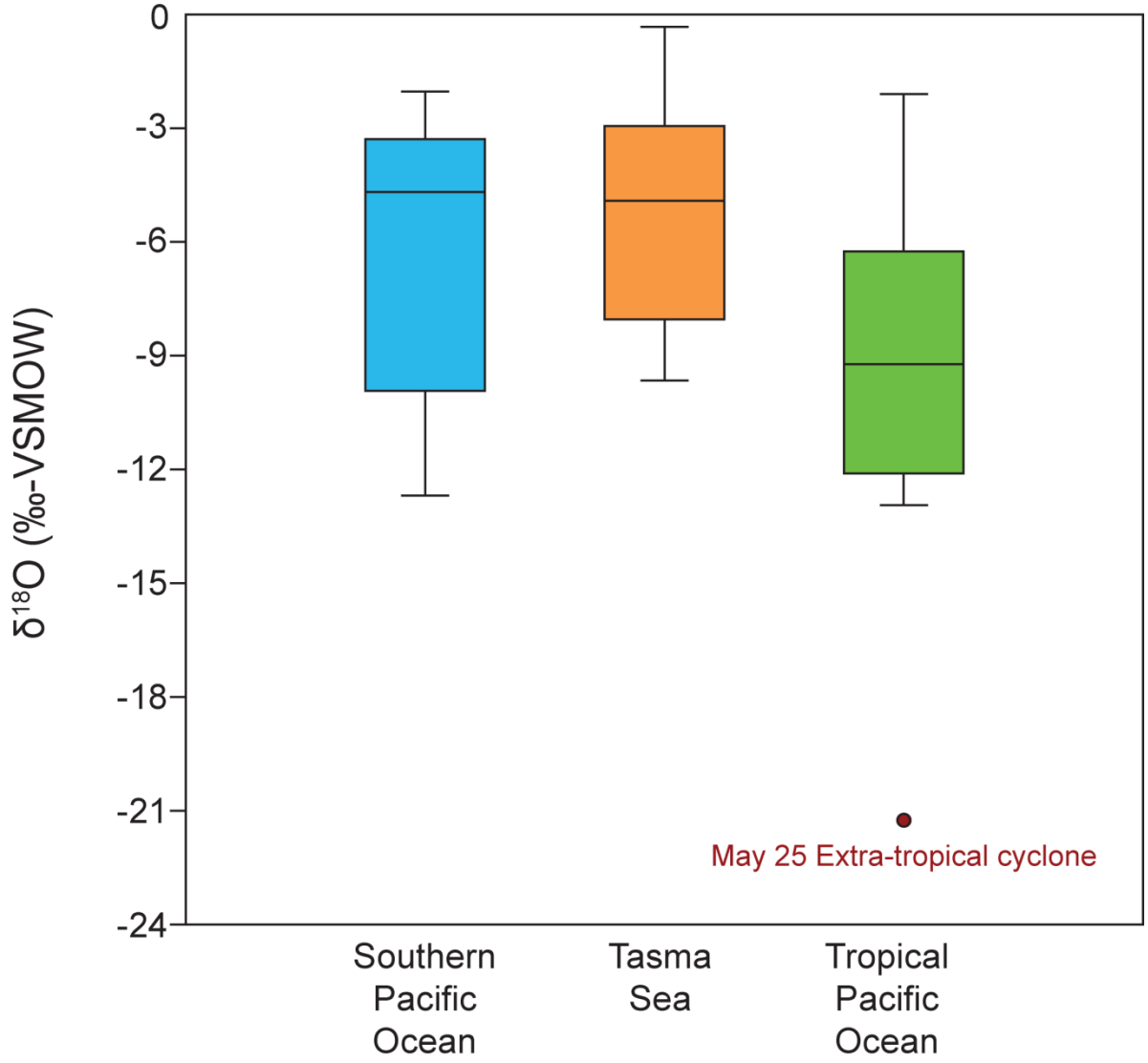

Figure 5.3: Box-plot distributions for δ18O values for precipitation events associated with respective moisture source

For each regional sector, a linear regression was fitted to the associated δD and $\delta^{18}O$ values to create individual meteoric water lines (Figure 5.4). The slopes of these LMWLs vary. Differences between LMWL y-intercept values also vary. This can also be seen in the relationship between how these LMWL lie with respect to the GMWL. For example, the local meteoric water line for the Southern Pacific Ocean (LMWL-SP) plots very close to the GMWL. However, the meteoric water lines for the Tasman Sea (LMWL-TS) and Tropical Pacific Ocean (LMWL-TP), however plot to the right of the both the GMWL and LMWL-SP.

This observation is consistent with similar analyses at tropical and sub-tropical island sites where the *d* (i.e. y-intercept) is more negative than the GMWL due to the meteoric water isotopic amount effect (Dansgaard, 1964).

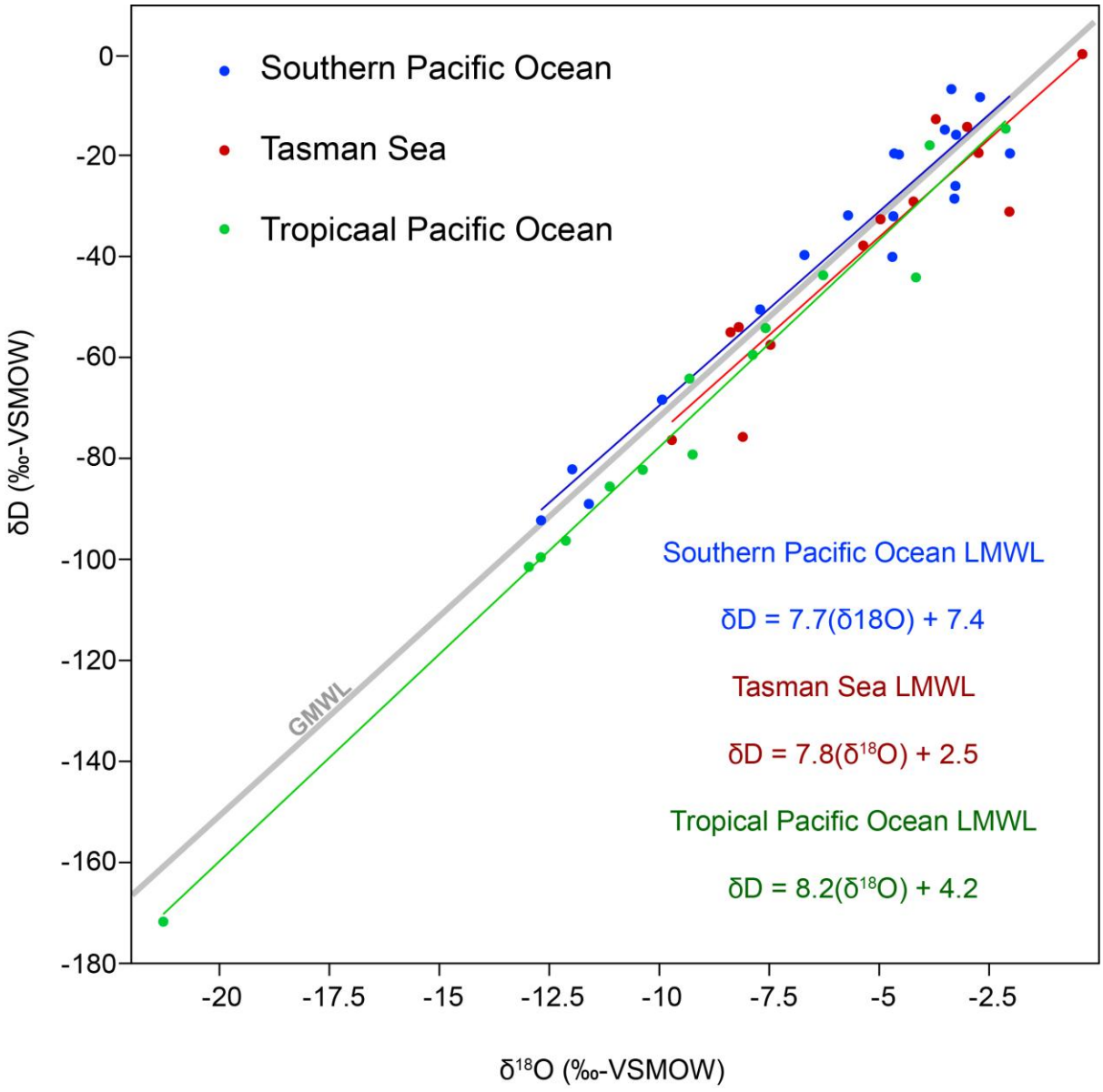

Figure 5.4: LMWLs derived for moisture source specific areas.

The positions of LMWLs suggest that there are differences with respect to the *d* of individual precipitation events between moisture sources. Box plots of the distributions of *d* between the different source areas show that for any air-parcel path, there is a large amount of variance (Figure 5.5). The Southern Pacific Ocean shows the most positive median *d* value (11 ‰), while the Tasman Sea (5 ‰) and Tropical Pacific Ocean (2 ‰) have correspondingly lower *d*

medians. The largest difference being between the Southern Pacific Ocean relative to the Tasman Sea and Tropical Pacific Ocean. These values agree well with the observation of the LMWL-SP plotting left of the LMWL-TP and LMWL-TS. These observations suggest that kinetic fractionation effects over the Southern Pacific Ocean are different than those of the Tasman Sea and Tropical Pacific.

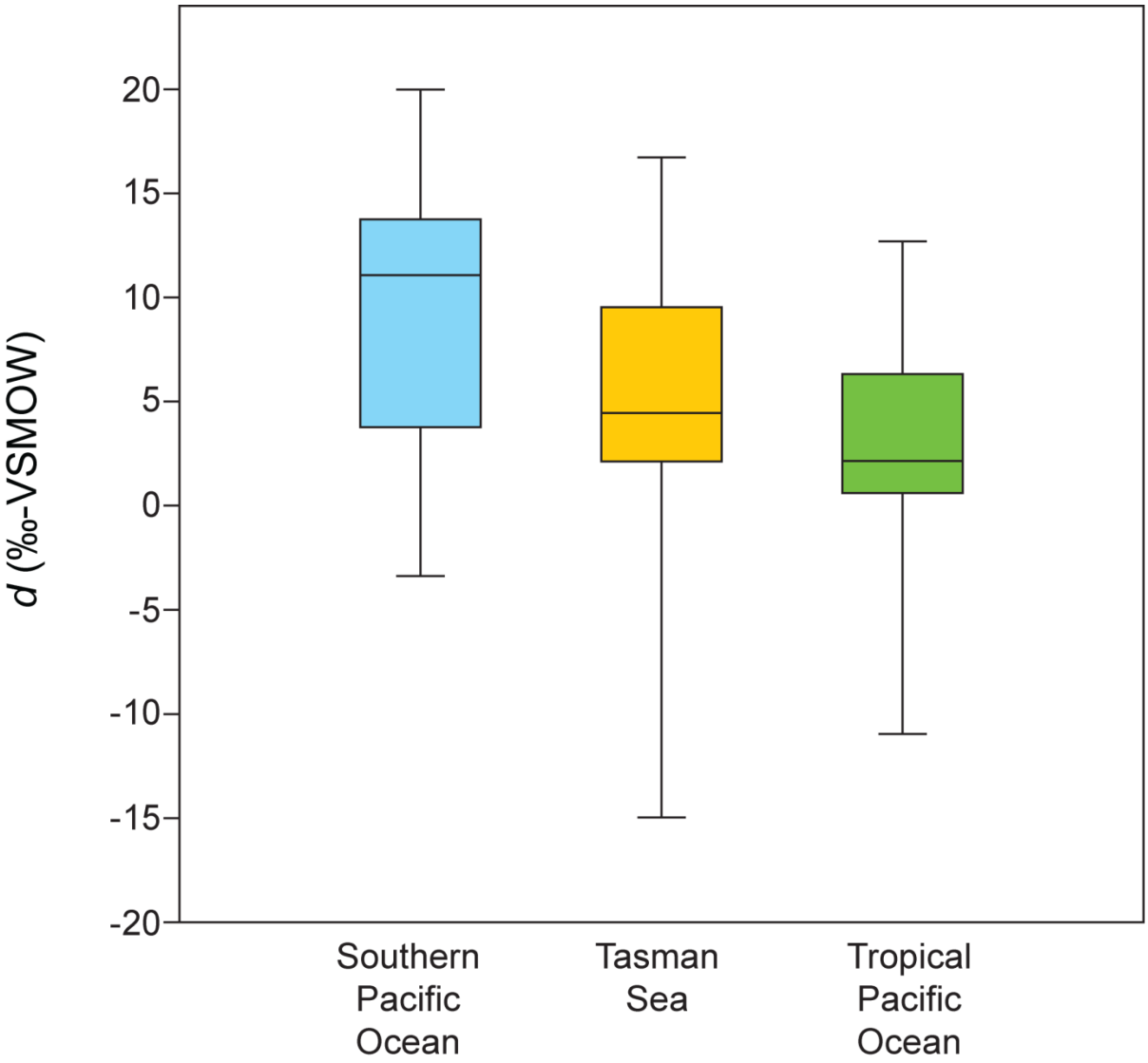

Figure 5.5: Box-plot of deuterium excess values for precipitation events from respective moisture sources

5.3.3. Derived Line-Conditioned Excess Calculations

Based on the methods presented by (Landwehr and Coplen, 2004) and further recommended by Gat (2010), line-conditioned excess ($LMWL_{excess}$) functions were developed for each of the LMWLs. A one standard deviation of $LMWL_{excess}$ from the LMWLs were also formulated. These are presented in Table 5.1. The line-conditioned excess values provide a

robust method in which to compare subsequent cumulative precipitation samples, surface waters, and groundwater to specific moisture origins.

Moisture Source	$LMWL_{excess}$	$LMWL_S$
Southern Pacific Ocean (LMWLSP)	$LMWLSP_{excess} = \delta D - 7.7\delta^{18}O - 7$	$LMWLSP_S = (\delta D - 7.7\delta^{18}O - 7)/1.8$
Tasman Sea (LWMLTS)	$LMWLSP_{excess} = \delta D - 7.8\delta^{18}O - 2$	$LMWLSP_S = (\delta D - 7.8\delta^{18}O - 2)/1.8$
Tropical Pacific Ocean (LMWLTP)	$LMWLSP_{excess} = \delta D - 8.2\delta^{18}O - 4$	$LMWLSP_S = (\delta D - 8.2\delta^{18}O - 4)/1.9$

Table 5.1: $LMWL_{excess}$ and $LMWL_S$ calculations for respective moisture sources

5.3.4. Relationships with Meteorological Conditions

Average local meteorological conditions were compared with measured stable isotope compositions through bivariate analysis. This was done by obtaining the meteorological conditions from NIWA's National Climate Database (http://cliflo.niwa.co.nz/) for the time intervals precipitation was collected and calculating a mean value. The meteorological conditions observed were surface temperature, relative humidity, rainfall amount (hourly), evaporation (Penman evapotranspiration), and wind direction.

A weak negative correlation ($R^2 = 0.14$) was observed between $\delta^{18}O$ and the mean amount of precipitation for a given sampling interval (Figure 5.6). However, no other significant trends are observed with respect to $\delta^{18}O$. A weak negative correlation ($R^2 = 0.22$) is observed between *d* and the mean temperature, however no other significant trends were observed with respect to *d*.

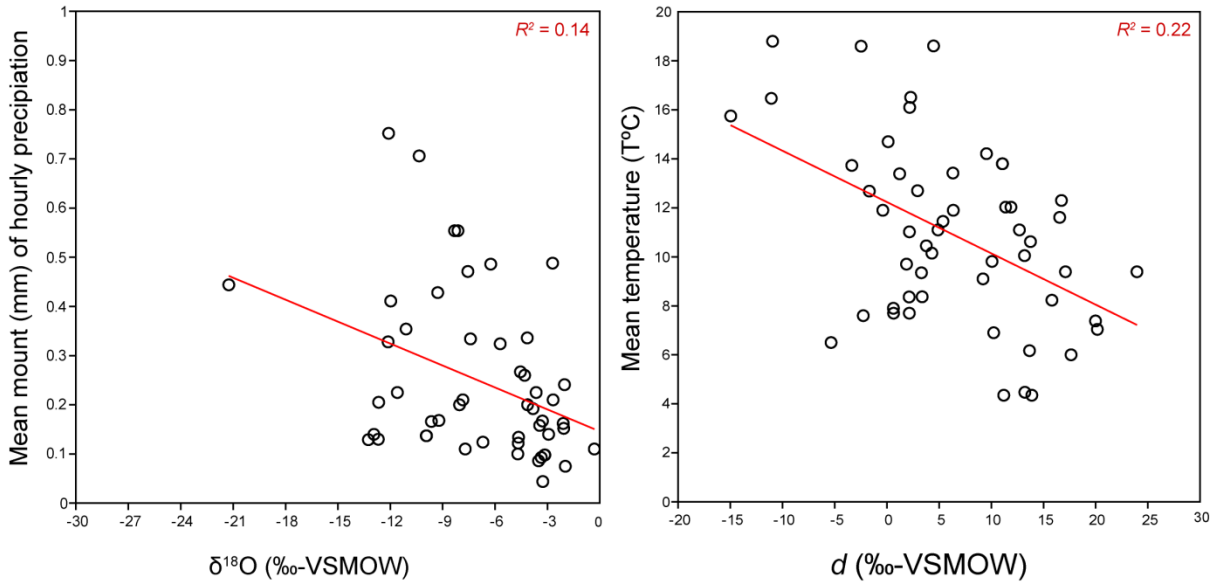

Figure 5.6: Weak relationships observed between $\delta^{18}O$ and mean amount of hourly precipitation and *d* and mean temperature

5.4. Isotopic Variability during Tropical Cyclones

5.4.1. May 25-28 Events

On 25 May, an extra-tropical cyclone source from the Tropical Pacific began to move over Christchurch. Sampling in Christchurch commenced at 12:00 PM, 25 May. Samples (IDs 47-54) were collected until 0:00, 28 May. Sampling, however, was not continuous. Back-trajectory analysis indicates that the earliest sample's (ID 47) moisture source, is most likely the Tropical Pacific. However, as the cyclone moved south-southeast, subsequent back-trajectories show moisture sourced from the Tasman Sea briefly, but then returning to a more Tropical to sub-Tropical Pacific origin (ID 48-52). In stark contrast, the last three samples (ID 53-54) originate from the Southern Pacific Ocean. See Appendix 3 for back-trajectories of this complex event.

The isotopic composition of this event goes from an extremely negative -172, -21.3 ‰ (δD and $\delta^{18}O$, respectively) to a more positive -51, -7.7 ‰. Moreover, there is also a large positive shift in *d* over the course of this event, as well. With the onset of high-intensity rainfall as the low-pressure system moved over Christchurch, the most negative value is observed. High-intensity rainfall occurs during the second sampling; however the isotopic composition is relatively more positive -97, -12.13 (δD and $\delta^{18}O$, respectively) suggesting recharge of air mass moisture has occured. Rainfall intensity remains relatively low through

ID 48-54 and becoming isotopically more positive. During the first duration of high intensity precipitation 8:00AM, 25 May to 6:00 PM, 25 May, wind direction changed dramatically from a southwesterly origin to easterly origin from approximately 12:00 PM to 4:00 PM. This change only lasted 3 to 4 hours before returning to predominantly south-westerlies; however it coincides with the time interval that the most negative δD and $\delta^{18}O$ is observed.

5.4.2. June 6-7 Events

On 6 June, another extra-tropical cyclone sourced from north and west of New Zealand, partly from the Tropical Pacific and the Tasman Sea began to move over Christchurch. Similar to the cyclone in May, substantial rainfall occurred over much of New Zealand, particularly, the eastern North Island. Sampling commenced at 10:30 AM, 6 June and was carried out until 10:30 PM, 7 June. Samples however were not collected back-to-back, but in 5 different intervals. From back-trajectory analysis, it is difficult to discern the origin from the 500, 1500, to 2500 meter simulations. At 500 meters trajectories tend to originate from Tropical-sub-Tropical Pacific until the final simulations where origins appear more from the Southern Pacific Ocean. At the 2500 meters, early simulations originate from the northern Tasman Sea and progressively originate more from the Tropical Pacific. This is likely the result of the low-pressure system moving eastward. 1500 meter trajectories generally fall between the 500 and 2500 meter trajectories. See Appendix 3 for back-trajectory results of this complex 4-dimensional event.

The $\delta^{18}O$ composition of this event ranged from -13.0 to -9.2 ‰. Unlike the May 25-28, the δD and $\delta^{18}O$ compositions evolve from more positive to negative and then from more negative to positive δ-values through time. However, similar to the May 25-28 event, *d* increases through time from -5 to 10 ‰, suggesting a more tropical sub-tropical source at the onset, but becoming predominantly more sourced from the Southern Pacific Ocean in the later samples.

5.5. Summary

A key result original to this thesis is the documentation of the large variability in the isotopic composition of Christchurch precipitation at the event scale. Back-trajectory analysis suggests that there are 3 major sources from which air moisture might originate. These are the Tasman Sea, the Tropical Pacific, and the Southern Pacific ocean. LMWLs derived for each of these regions are similar in slope, but have very different y-intercept values. The Tasman Sea and Tropical Pacific plot similarly to previously documented tropical zones, while the

Southern Pacific Ocean plots similarly to the GMWL. From these LMWLs, $LMWL_{excess}$ functions were calculated to compare subsequent data from cumulative precipitation, surface waters, and groundwater to specific air-parcel paths. Weak negative correlations were observed between $\delta^{18}O$ and the mean amount of precipitation ($R^2 = 0.14$) and between the *d* value and the mean temperature ($R^2 = 0.22$) for a given sampling interval. For the two extra-tropical cyclones sampled, isotopic compositions are relatively much more negative than the majority of δD and $\delta^{18}O$ and shifts in the *d* through the events became increasingly more positive.

Chapter 6 : Isotopic and Physical Variability of Surface Water and Groundwater Interactions

6.1. Introduction

In addition to the meteoric water stable isotopic results presented in Chapter 5, two additional sets of rainfall isotopic compositions, at the monthly scale, are available for Christchurch (Taylor, 1990; Stewart et al., 2002). Taylor (1990) collected monthly precipitation from February 1984 to December 1988 and these samples were analysed for δD and $\delta^{18}O$ compositions. Stewart et al. (2002), collected cumulative surface rainfall and lysimeter infiltration samples at variable time intervals (i.e. generally monthly) from June 1999 to January 2005 at the Christchurch International Airport, predominantly for $\delta^{18}O$ only. Of the 61 samples from Stewart et al. (2002) collected for cumulative surface rainfall and the 35 lysimeter infiltration samples (infiltration was not always present), a total of 9 samples (5 for rainfall, 4 for infiltration) samples were analysed for δD and $\delta^{18}O$. As Taylor (1990) and Stewart et al. (2002) do not discuss the variations of these isotopic compositions at length, a detailed interpretation is presented here. Three monthly cumulative surface rainfall samples that were collected at the University of Canterbury for April, June, and July 2010, analysed for δD and $\delta^{18}O$, and are included with the combined cumulative surface rainfall analysis. Waimakariri River $\delta^{18}O$ samples are presented both from this study and Taylor et al. (1989). The majority of groundwater $\delta^{18}O$ values originate from the ECan water quality database with some $\delta^{18}O$ values for springs used, as well. Combined δD and $\delta^{18}O$ compositions for springs and groundwater are from UCSIF analyses.

Section 6.6 presents an analysis of δD and $\delta^{18}O$ composition as $LMWL_{excess}$. From these analyses, a quantitative approach is used to define surface and groundwater relationships to air-parcel paths and to assess their utility in determining relative recharge contributions based relationships to LMWLs. Relative contributions were then calculated using $\delta^{18}O$ end member compositions in a single-isotope binary mixing model.

This chapter concludes with interpreted groundwater flow paths determined from potentiometric surfaces calculated from the average groundwater level for wells in the CGS and Central Canterbury Plains from 2006-2010 for comparison against interpretations made from the distribution of $\delta^{18}O$ values.

6.2. Cumulative Surface Rainfall

6.2.1. Cumulative Surface Rainfall (Taylor, 1990)

δD and $\delta^{18}O$ compositions of cumulative surface rainfall collected at the Christchurch International Airport (Taylor, 1990) show nearly as much variability as single precipitation event samples, excluding the extremely negative δD and $\delta^{18}O$ values from extra-tropical cyclone event of 25-28 May. $\delta^{18}O$ compositions range from -13.7 to -3.5 ‰. In general, δ-values are more positive in the summer months (December-January-February) and more negative in winter months (June-July-August). Moreover, variance in monthly values is higher in the winter months. The weighted-mean annual $\delta^{18}O$ composition of precipitation from Taylor (1990) is calculated to be -7.4 ‰, which is more negative than the Bowen-Wilkensen Global Model of $\delta^{18}O$ for modern precipitation for the Christchurch Airport site (-6.5 ± 0.3 ‰) (Bowen and Revenaugh, 2003; Bowen, 2011). Deuterium excess values also show seasonal trends whereby more positive *d* values are observed during the winter months similar to the median values and y-intercept of the Southern Pacific Ocean, while during the summer months, *d* values are relatively lower and similar to median and y-intercept observed for the Tasman Sea and Tropical Pacific.

Weak positive correlations are observed between the $\delta^{18}O$ values of monthly precipitation and monthly means of temperatures (R^2 = 0.14) and evapotranspiration (R^2 = 0.14) (Figure 6.1). Also, weak negative correlations are observed between monthly *d* values and monthly mean temperature (R^2 = 0.15) and evapotranspiration (R^2 = 2.3). Notably, a similar relationship is observed between *d* and temperature for precipitation at the event-scale. There no observable correlations between $\delta^{18}O$ or *d* and the Southern Oscillation Index, Pacific Decadal Oscillation, or El Nino-La Nina climate indices.

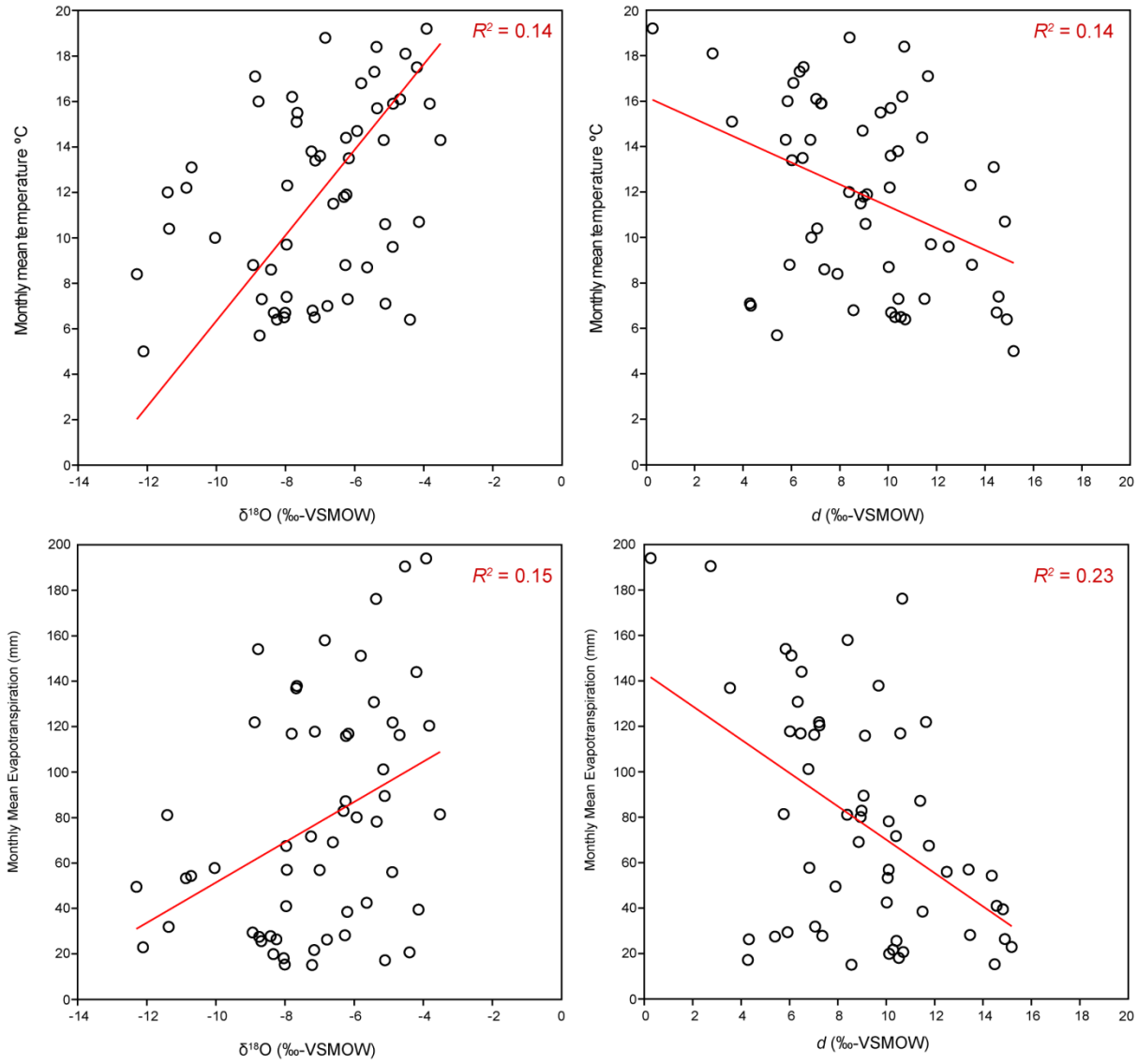

Figure 6.1: Relationships between monthly isotopic compositions and monthly mean temperature and evapotranspiration

These observations are particularly relevant in interpreting paleoclimate proxies with respect to climate-isotope relationships for the east coast of the South Island. Moreover, these observations are important in understanding the potentials controls on the variability of end-member stable isotope compositions related to surface rainfall in the CGS and tracing surface water and groundwater interactions.

6.2.2 Cumulative Surface Rainfall (Stewart et al., 2002)

Collections periods from Stewart et al. (2002) do not always correspond to beginning and end of calendar months (Appendix 2). For this thesis, the determination of a month to associate with a δ-value was done such that the date in the middle of a collection period would be the

selected month. Regardless, Stewart's samples ranged between -12.6 and -1.9 ‰ for $\delta^{18}O$ values (Stewart et al., 2002). These are similar ranges of $\delta^{18}O$ observed in precipitation events collected in this study and those of Taylor (1990). Similar seasonal patterns are also observed in the Stewart et al. (2002) dataset as those described above from Taylor (1990).

6.3. Lysimeter Infiltration (Stewart et al., 2002)

$\delta^{18}O$ values for lysimeter infiltration samples (Stewart et al., 2002) show less variation than surface rainfall, ranging from -10.6 to -4.0 ‰. As observed in the surface rainfall data, there is an overall trend of more negative $\delta^{18}O$ values in winter months with relatively more positive $\delta^{18}O$ values observed in the summer months indicating water movement through the vadose is likely rapid. Notably, fewer samples were collected in the summer months as evapotranspiration rates are higher at this time and combined with relatively lower rainfall amounts in summer months, there is ultimately less meteoric water infiltration. The weighted mean-annual $\delta^{18}O$ composition of lysimeter infiltration is -6.7 ‰, 0.7 ‰ more positive than the annual mean calculated for surface rainfall.

6.4 Waimakariri River

Taylor et al. (1989) discuss in some detail variations in both the $\delta^{18}O$ composition and ion chemistry of the Waimakariri River. However, these prior isotope analyses report $\delta^{18}O$ only. As part of this study, 5 Waimakariri samples, collected in March and July 2010, were analysed for both δD and $\delta^{18}O$. $\delta^{18}O$ values exhibit less variation than both precipitation (event and cumulative collection) and lysimeter infiltration. The Waimakariri samples original to thesis range between -9.9 and -8.2 ‰. $\delta^{18}O$ values from Taylor et al. (1989) range between -10.6 and -7.7. As observed in precipitation, $\delta^{18}O$ values for Waimakariri River generally oscillate seasonally.

6.5. Groundwaters and Avon River springs

$\delta^{18}O$ compositions for groundwater samples obtained from the ECan Water Quality Database collected during 2006-2010 show far less variation than precipitation and lysimeter infiltration. $\delta^{18}O$ values from Aquifer 1 range between -9.3 and -8.0 ‰. For Aquifer 2, $\delta^{18}O$ values range between -9.5 and -8.2 ‰. Similar median values are observed for Aquifer 1 (-8.8 ‰) and Aquifer 2 (-8.9‰). For the deeper aquifers (Aquifers 3 to 5), $\delta^{18}O$ range between -9.3 and -8.76 ‰ with a median value of -9.2 ‰. With deeper aquifers, the upper ranges and median $\delta^{18}O$ median values for groundwater samples decrease. For the 9 wells analysed for δD and $\delta^{18}O$, *d* values ranged between 7 and 11‰ with a median value of 9 ‰.

$\delta^{18}O$ values of grab samples collected during March 2010 for surface waters in the Avon River Springs System range between -10 and -8.2 ‰ with a median value of -9.0 ‰. These values agree well the observed ranges and median value for groundwater samples from Aquifer 1. Deuterium excess values range between 6 and 12 ‰ with a median value of 11 ‰.

6.6. Comparison of Surface Waters and Groundwater to Atmospheric Origins

To elucidate the relationships between atmospheric moisture sources and cumulative surface rainfall, surface waters, and groundwater in the CGS, $LMLW_{excess}$ calculations were made to assess the deviation of δD and $\delta^{18}O$ values for each dataset against each of the separate LMWLs. For example, deviations of the average δD and $\delta^{18}O$ for monthly surface rainfall measured by (Taylor, 1990) were measured against the three LMWLs derived for the Southern Pacific Ocean, Tasman Sea, and Tropical Pacific Ocean. From Figure 6.2, it is observed that the smallest δD and $\delta^{18}O$ deviations are associated with the Southern Pacific Ocean. This suggests the source of moisture contributing to precipitation over the CGS to be predominantly from the Southern Pacific Ocean, particularly during the winter months. During the summer months, deviations from the Southern Pacific Ocean are more negative, which is apparent by δD and $\delta^{18}O$ showing less deviation relative to the Tasman Sea and Tropical Pacific Ocean LMWLs. This suggests that for the summer months, moisture contributions from the Tasman Sea and Tropical Pacific Ocean are at their highest.

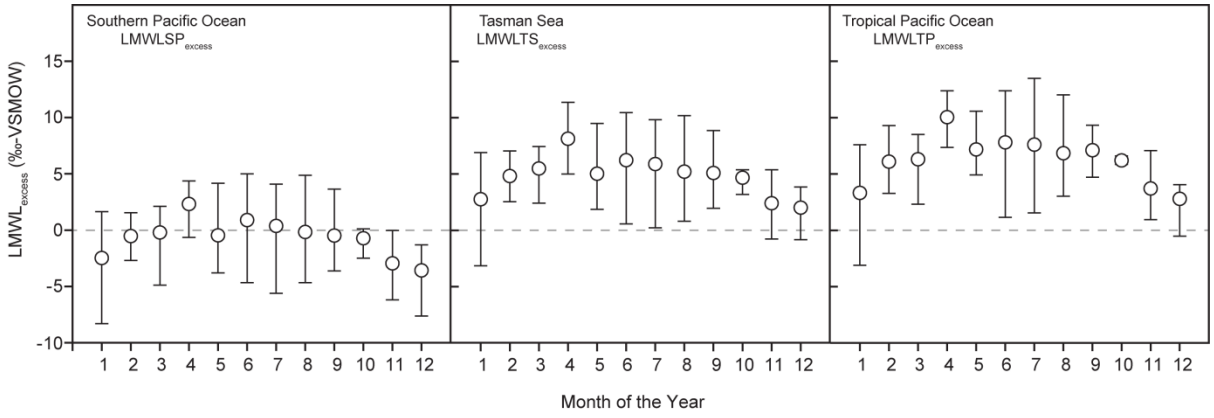

Figure 6.2: LMWLexcess deviations for mean monthly rainfall calculated for each moisture origin. The '0' line represents no deviation.

Datasets for groundwater and the Avon River springs also show the smallest amount of deviation for δD and $\delta^{18}O$ values to be associated with the LMWL for the Southern Pacific Ocean, as well. There are relatively few δD and $\delta^{18}O$ values for the lysimeter infiltration and

the Waimakariri River (4 and 5, respectively). However, lysimeter infiltration and the Waimakariri show deviations to be lowest around the LMWL for the Southern Pacific Ocean.

These observations suggest the predominant atmospheric source of moisture to surface rainfall and lysimeter infiltration in the CGS, the Waimakariri River, the Avon River springs, and groundwater in the CGS to be from the Southern Pacific Ocean. However, inferring any distinction between surface rainfall and lysimeter infiltration in the CGS, the Waimakariri River, the Avon River springs, and groundwater based on LMWLs as done by Weyhenmeyer (2002) are not apparent qualitatively. Furthermore, a mixing model would likely be unable to resolve contributions to the Avon River springs and groundwater derived from Waimakariri River channel leakage and lysimeter infiltration based on any quantitative deviations from LMWLs. However, the differences between the $\delta^{18}O$ compositions of the Waimakariri River and surface rainfall and lysimeter infiltration would likely prove useful in a linear mixing model.

6.7. $\delta^{18}O$ Mixing Model

A binary mixing model using $\delta^{18}O$ values of land surface recharge (monthly surface rainfall (Taylor, 1990) and lysimeter infiltration (Stewart et al. 2002) and the Waimakariri River (Taylor et al., 1989) was used to assess relative contribution to the Avon River springs system. The underlying assumption to this model was that the contributions were from two isotopically distinct end-members. Using a Shapiro-Wilk test, normal distributions are observed for the monthly surface rainfall (p(normal) = 0.052) and lysimeter infiltration (p(normal) = 0.99), but not for the Waimakariri (p(normal) = 0.007). A non-parametric Mann-Whitney test performed between the Waimakariri and surface rainfall observes the medians between these two datasets to be significantly different (p = < 0.0001). A second Mann-Whitney test performed between the Waimakariri and lysimeter infiltration also observed the medians between these two datasets to be significantly different (p = < 0.0001). Based on the significant differences between the end-member compositions, the model then used to calculate contributions based on: 1) monthly surface rainfall and Waimakariri River leakage and from 2) lysimeter infiltration and Waimakariri River leakage.

Using monthly surface rainfall and Waimakariri River leakage, the model calculates contributions from the Waimakariri River to be 79 % ± 7 % to the Avon River springs. However, these observations do not record the actual water moving through the vadose zone, ultimately contributing to groundwater recharge. To characterize contributions to the Avon

River springs using water that has moved through the vadose zone, lysimeter infiltration must be used. Using the lysimeter infiltration and the Waimakariri as end-members, contributions from the Waimakriri River to the Avon River springs were shown to be 85 % ± 6 %. The differences between these two estimates are within error of one another. Much of the variance associated with these estimations are inherent in the isotopic variability of precipitation and infiltration. Ultimately, the lysimeter infiltration data most likely yield more accurate recharge values as this is actual water passing through the vadose zone.

We compared these results to recharge estimates from White (2009) where estimated baseflow for the Avon River springs was calculated to be ~80 %. White's calculation was based on the average infiltration of precipitation to be 30 % of the annual precipitation amount. In terms of volume, infiltration over the Avon Springs Catchment area is estimated to be 325 L/s and mean annual baseflow of the Avon River is estimated to be 1697 L/s. From these estimations, 20 % of baseflow can be account for by infiltration. These observations agree well with the modelled contributions from both mixing models. Considering this, $\delta^{18}O$ distributions in groundwaters near the Waimakariri River and Avon River springs should show relatively more negative $\delta^{18}O$ values.

In Aquifers 1 and 2, near the Waimakariri River and Avon River springs, relatively more negative $\delta^{18}O$ values are observed (Figure 6.3). Towards the southwestern portion of the study area, $\delta^{18}O$ values become increasingly more positive, suggesting a change from Waimakariri River dominated recharge to increased amounts of recharge from rainfall infiltration. In Aquifer 2, towards the coast, more negative $\delta^{18}O$ values are observed, however towards the southwestern portion of the study area, more positive $\delta^{18}O$ values are observed, similar to Aquifer 1. With depth in the CGS, $\delta^{18}O$ values generally decrease (see Appendix 2). This would suggest that Waimakariri River losses recharge deeper aquifers, as well, an observation pointed out in previous studies (Stewart et al., 2002; Hanson and Abraham, 2009). Groundwater flows paths in deeper aquifers should then indicate groundwater movement moving away from the Waimakariri River.

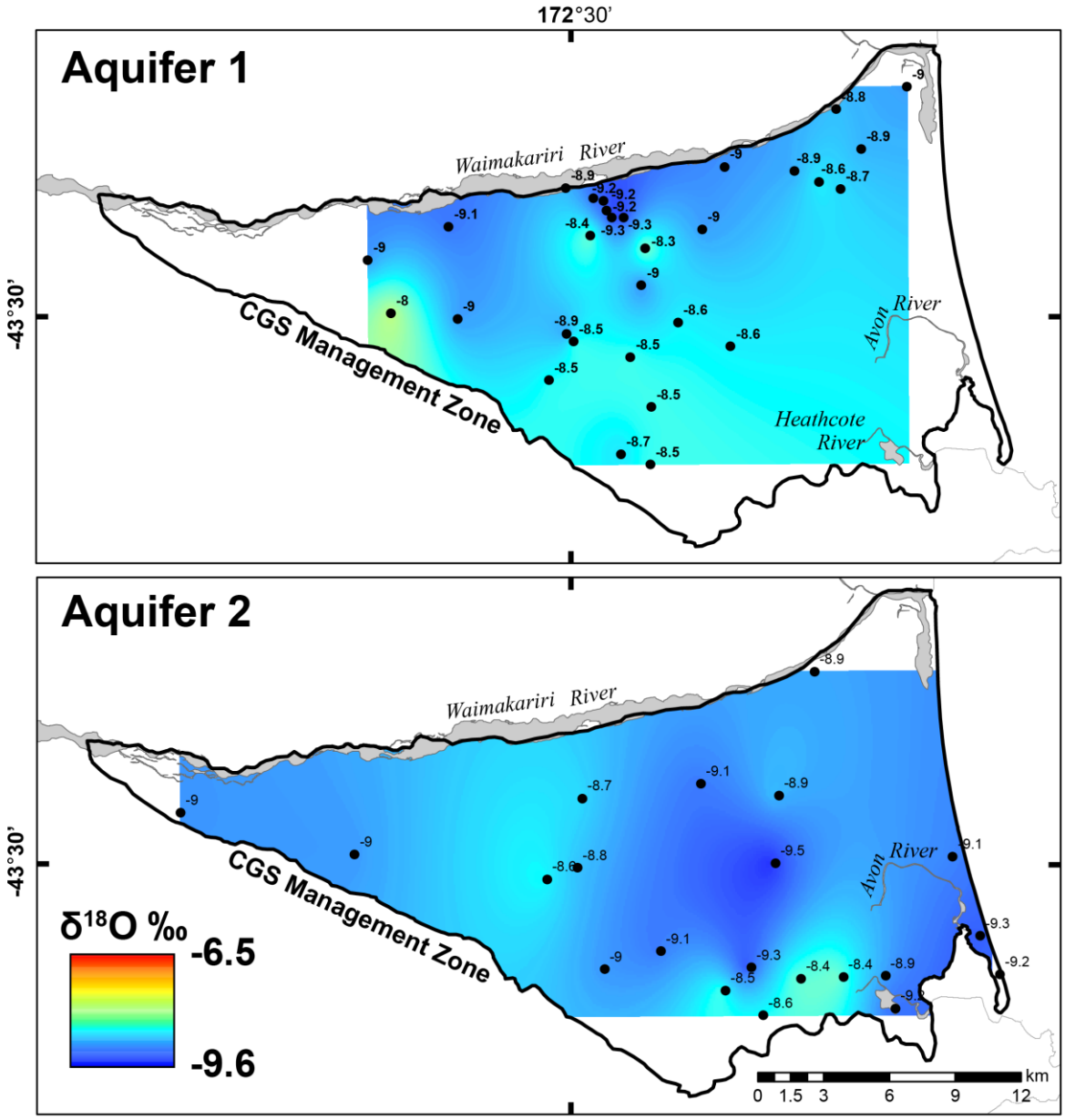

Figure 6.3: Distribution of $\delta^{18}O$ values in groundwater samples from Aquifer 1 and Aquifer 2

6.9. Deep Groundwater Flow

Interpreted deep groundwater flow paths derived from wells both in the CGS and in the Central Canterbury Plains are shown in Figure 6.4 for Aquifer 4. Groundwater flow paths at the Central Canterbury Plains-CGS boundary near Banks Peninsula suggest groundwater flows from the Central Canterbury Plain in to the CGS. These results suggest that with depth in the CGS, groundwater flow paths change. However, resolving the relative contribution to these wells from Waimakariri recharge and from inland infiltration are not possible at this

time. It is unclear whether the groundwater flowing to these wells is from the upper reaches of the Waimakariri River or potentially from much further inland.

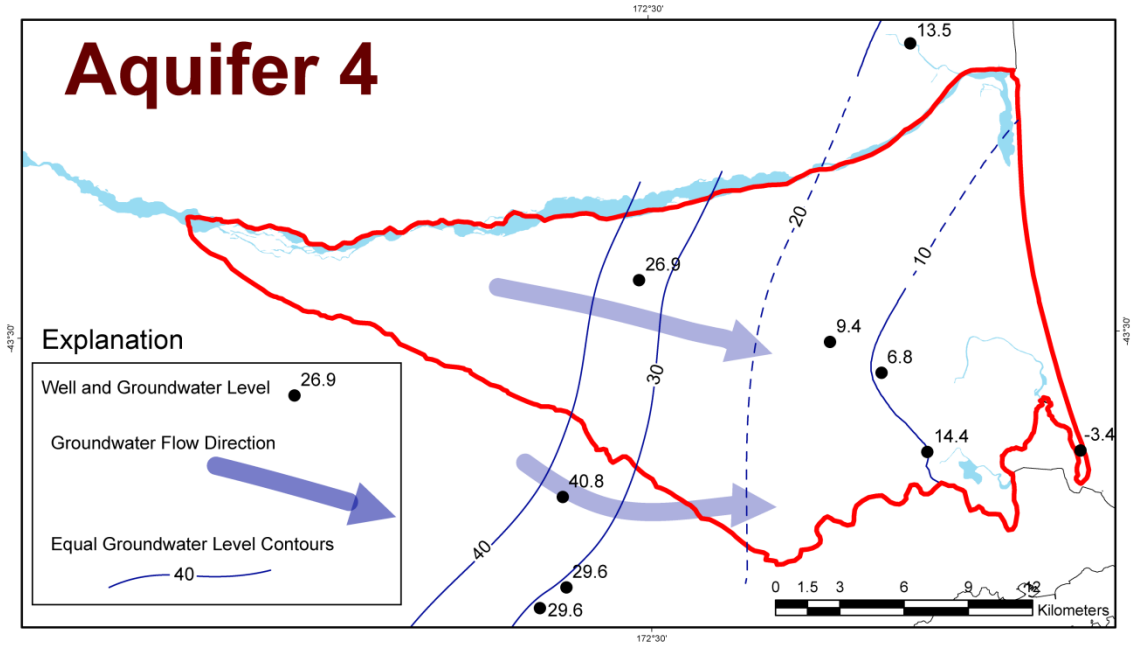

Figure 6.4: Interpreted groundwater flow paths from the Central Canterbury Plains to the CGS. CGS boundary in red outline

6.10. Summary

$\delta^{18}O$ and *d* values from monthly surface rainfall (Taylor, 1990) exhibit seasonal trends. Weak positive correlations are observed between $\delta^{18}O$ values and monthly mean surface temperature and monthly mean evapotranspiration (R^2 = 0.14 and 0.14, respectively). Weak negative trends are also observed between *d* and monthly mean surface temperature (R^2 = 0.15) and between d and evapotranspiration (R^2 = 0.23). No relationships are observed between monthly isotopic compositions and climatic indices (i.e. SOI, PDO, and ENSO). It is inconclusive from these data what the main drivers are with respect to the monthly isotopic composition of surface rainfall over the CGS

Cumulative surface rainfall collected at the Christchurch International Airport reported in Taylor (1990) and Stewart et al. (2002) both show similar ranges in the $\delta^{18}O$ values of cumulatively collected precipitation and display seasonal trends. $\delta^{18}O$ values for lysimiter infiltration range less respect to positive and negative end-member compositions relative to monthly surface rainfall, however do show seasonal trends like the surface rainfall, which suggest relatively fast travel through the vadose zone. From Taylor et al. (1989), $\delta^{18}O$

compositions of the Waimakariri River varies seasonally. Relative to precipitation and infiltration on the collected in the CGS varies only slightly (± 3 ‰). $\delta^{18}O$ compositions of the CGS and the Avon River springs show relatively similar ranges to the Waimakariri River and similarly have small ranges in comparison with monthly precipitation and infiltration.

All δD and $\delta^{18}O$ measurements were tested against the three lc-excesses derived for each LMWL and show that for precipitation, surface water, and groundwater, the least amount of deviation occurs with respect to the Southern Pacific Ocean LMWL. These relatively small deviations, however do not yield *d* or $LMWL_{excess}$ as a good tracer of surface/groundwater interactions.

Statistically significant differences ($p = < 0.0001$), however, are observed between monthly surface rainfall and the Waimakariri River and lysimeter infiltration and the Waimakariri River. Using these data as end-member compositions in a binary-single isotope mixing model, I calculated relative Waimakariri River contributions to the Avon River springs to be approximately 79 % ± 7 % (using monthly surface rainfall) and 85 % ± 6 % (using lysimeter infiltration). Both these estimates agree well with a previous physical mass balance model to the Avon River springs catchment by White (2009) where White estimated 80 % of recharge to the Avon River springs originated from the Waimakriri.

Spatially, more negative $\delta^{18}O$ values are observed in groundwater samples near the Waimakariri River and near the Avon River springs, which agree well the mixing model. More negative compositions are also observed along the eastern margin of the CGS at the coast. Near Banks Peninsula and along the south-western boundary, more positive isotope compositions and higher ion concentrations are observed, which indicate increased recharge from precipitation. $\delta^{18}O$ values indicative of Waimakariri recharge are observed in deeper aquifers.

At deeper depths, groundwater appears to flow from the inland plains to the CGS, which suggests relatively more negative $\delta^{18}O$ entering the CGS from the Central Canterbury Plains, which may be sourced from the upper reaches of Waimakariri or from the foothills of the Southern Alps.

Chapter 7 : Discussion

7.1 Introduction

This chapter presents a discussion of the findings from this thesis on:

1. The isotopic variability of Christchurch precipitation events and relationships to meteorological conditions
2. Local meteoric water lines and corollaries with atmospheric moisture sources
3. Isotopic variability of Tropical Cyclones and their relationship to surface waters
4. The isotopic variability of monthly precipitation and its relationship to atmospheric sources, long-term means, and surface waters
5. Stable isotope composition of surface waters contributing recharge
6. Characterizing shallow groundwater recharge to the Avon River springs
7. Groundwater recharge to deeper aquifers of the CGS

7.2. Why Such Large Isotopic Variability in Precipitation Events?

As shown in section 5.2. the stable isotopic composition of Christchurch precipitation events varies over 20‰ for $\delta^{18}O$ and over 170‰ for δD. For context, a similar range occurs across the whole of North America spanning Alaska to Florida at monthly time-scales. Weak positive covariance between $\delta^{18}O$ and the mean hourly rainfall amount (R^2 = 0.15) are apparent. A weak negative co-variation between *d* values and mean temperature (R^2 = 0.23) is also present, indicating a linkage between the partial evaporation of rain drops beneath the cloud base layer and temperature which condensation took place (Stewart, 1975; Friedman et al., 2002). These patterns suggest that with higher temperatures there is increased aridity, thus lower *d* values as also seen by Tian et al. (2007). Ultimately, meteorological conditions during precipitation collection are linked to the isotopic fractionation processes occurring in air parcels. The *d* values for precipitation in Christchurch are likely controlled by both the initial evaporative conditions of water vapour using a Craig & Gordon (1965) model and are subsequently modified by atmospheric conditions during precipitation at the collection site (Stewart, 1975). The predominance of either factor for each individual event is a highly-complex phenomenon out of the scope of this study, but is recognized.

7.3. Local-Meteoric Water Lines for Christchurch Precipitation

Back-trajectory analysis reveals that, on a regional scale, air parcels delivering precipitation to Christchurch originate from one of three areas: the Tropical Pacific Ocean, the Tasman Sea, and the Southern Pacific Ocean. This zonal classification agrees well with atmospheric patterns associated with the 40º S latitude belt of westerly anti-cyclones, troughs from the poleward regions, and divergent easterlies from the equatorial regions (Lorrey et al., 2008). LMWLs were derived for precipitation events having been sourced from the Southern Pacific Ocean, Tasman Sea, or the Tropical Pacific Ocean. Observations by Dansgaard (1964) show that for tropically to sub-tropical sourced moisture, LMWLs may pass through or very close to SMOW. This pattern exists when the moisture is sourced from areas with relatively high evaporation rates (Sharp, 2007). The LMWLs derived for the air-parcel source regions of Christchurch precipitation do not pass through SMOW ($\delta D = 0‰$), but their y-intercept values are lower than the GMWL y-intercept. The LMWL for the Southern Pacific Ocean has the most positive y-intercept ($\delta D = 7‰$). However, the LMWLs for the Tasman Sea and the Tropical Pacific Ocean have lower y-intercepts (3 and 4‰, respectively). It is inferred that the tropical to sub-tropical moisture sources associated with the Tropical Pacific Ocean and Tasman Sea tend to have lower deuterium excess values due to condensation occurring at relatively high humidity (>80%) and high evaporation rates. However, their overall slope is similar to the GMWL as their isotopic compositions are likely strongly influenced by Rayleigh processes during moisture transport to the CGS area.

The Southern Pacific Ocean (LMWL-SP) has a similar slope (slope = 7.6) to the GMWL (slope = 8.0). Also, this LMWL lies very close to the GMWL indicating its *d* is also similar to the GMWL y-intercept value. Its displacement to the left of the more tropical to sub-tropical moisture likely results from formation of water vapour at lower relative humidity (~ 80%) then moisture sourced from the tropical to sub-tropical regions (i.e. Tropical Pacific and the Tasman Sea). Moisture sourced from the Southern Pacific Ocean results from contributing evaporation primarily between 30º and 50ºS (Sodemann and Stohl, 2009). Subsequent transport of this moisture is carried by disturbed westerlies associated with the Southern Hemisphere Polar Jet (Archer and Caldeira, 2008) to both Antarctica and New Zealand, specifically Christchurch. It is no surprise then that similar *d* values are observed for some coastal locations in Antarctica (~ 160 to 180ºE) (Masson-Delmotte et al., 2008) and Christchurch, New Zealand as the moisture source regions coincide (Sodemann and Stohl, 2009). Antarctic precipitation, however, does have much more negative $\delta^{18}O$ values due to

temperature and latitude effects associated with Rayleigh distillation (Petit et al., 1991; Masson-Delmotte et al., 2008).

For LMWLs derived for Christchurch precipitation:

1. There is a stark difference between tropical to sub-tropical moisture sources and mid-latitude sourced moisture evident by the relative positioning of these LMWLs with the GMWL.
2. The positioning of the LMWLs are correspondent to associated *d* values of precipitation samples.
3. Deuterium excess values for tropical to sub-tropical and mid-latitude sources show similar patterns which are linked with the environmental conditions at the time water vapour formed as also evident by the relative positioning of the LMWLs.

It is stressed that underlying these observations are highly complex oceanic-atmospheric coupled processes that occur during precipitation events, but on a gross-scale show reasonably discernible patterns. Deuterium excess alongside $\delta^{18}O$ and δD values may prove useful in tracing surface water and groundwaters, with particular reference to atmospheric origins.

7.3.1. Tropical Cyclone Events

Interestingly, some of the most negative isotopic compositions observed during this study were associated with extra-tropical depressions. Notably, the extra-tropical depression that passed over Christchurch 25 May 2010 was when the most negative isotope composition was recorded. The anonymously negative composition may in part be related to both in-cloud processes associated with frontal convection, rainfall intensity, and Rayleigh distillation (Friedman et al. 2002; Miller et al. 2006). High intensity rainfall was recorded at the Kyle Street EWS station (NIWA climate station) during the precipitation collection period for this extremely negative $\delta^{18}O$ value (-21.3‰). Interestingly, these systems generally become more positive through time. This may be associated with the incorporation of water vapour sourced from the mid-latitudes that has not undergone extreme Rayleigh distillation as might have the tropically sourced moisture arriving at Christchurch.

Furthermore, as these low-pressure systems migrate south, back trajectory calculations suggest that the moisture source moves from tropical to sub-tropical sources to the Southern Pacific Ocean. Notably, *d* values generally become more positive with this shift. It is

therefore suggested that shift of moisture source apparent in the back-trajectories are intrinsically related to the shift in *d* values. Trajectories associated with the tropical to sub-tropical moisture source have lower *d* values, while moisture from the Southern Pacific Ocean has more positive *d* values. These inferences agree well with both the derived LMWLs and models of deuterium excess associated with environmental conditions during water vapour formation.

Ultimately, tropical cyclones' contributions to surface waters and groundwaters are important in tracing hydrologic fluxes on the event-scale. Resolving the incorporation of anomalous negative values such as the $\delta^{18}O$ value of -21.3‰ in more well-mixed systems however are unlikely.

7.4. Isotopic Composition of Monthly Precipitation over the CGS from Taylor (1990)

7.4.1. Monthly Variability

Monthly precipitation collected by Taylor (1990) show long-term average seasonal trends with respect to δD and $\delta^{18}O$ compositions. However, there is still relatively large variability in monthly isotopic composition for $\delta^{18}O$ (< 5‰).

Deuterium excess values and calculated $LMWL_{excess}$ values show the smallest amount of deviation relative to the Southern Pacific Ocean LMWL, seasonal trends indicate more positive negative excursions from this LMWL to occur during the summer months. These seasonal trends are likely associated with circulation changes in the Southern Hemisphere.

7.4.2. Climatic Corollaries

In the winter months, decreased solar radiative forcing over the tropical leads to diminished convective power of tropical to sub-tropical cyclone systems. In response, the tropical convergence zone migrates northward and is in part replaced by increased south westerly flow over the South Island. This may be attributed to the dominant Southern Pacific Ocean *d* value present in the winter months.

However, year-on-year, it is still important to remember large variations in circulation patterns exist, which deviate from seasonal patterns. This variability is apparent in the isotopic records as there are large ranges associated with the monthly average both for $\delta^{18}O$ and $LMWL_{excess}$ values. Similar to the event-scale variability, these variations are attributable to the complex oceanic-atmospheric interaction between equatorial and mid-latitude to polar

air masses, giving rise to very complex meteorological conditions over New Zealand both for synoptic, monthly, and annual time scales, which are manifested in the stable isotope data.

Under these pretences, a considerable amount of unexplained variance would likely be associated with any climatic signals or inputs into hydrologic systems. This is seen in the weak correlations observed between meteorological conditions and stable isotopic compositions. No significant co-variation between ENSO, SOI, and PDO and $\delta^{18}O$ and δD are observed, either (see Chapter 7). However, the lack of correlation does not necessarily rule out their existence as the data for Taylor (1990) represents only 4 years of collection with respect to decadal to multi-decadal climatic processes. Conversely, averages over the four-year period for monthly collections do show considerably strong relationships between the isotopic composition of precipitation and meteorological conditions. A subsequently larger dataset is critically needed to further test these observations. Advances in analytical technology, such as cavity-ring-down laser spectroscopy units, provide a faster, more cost-effective, and analytically precise solution for acquiring stable data across New Zealand at multiple spatial and temporal scales than traditional IRMS (see Chapter 4). Notably, the laser spectroscopy units are much more precise (±0.001‰) than IRMS. Understanding this variability is not only critical in determining relative contributions to surface and groundwaters, but also understanding the error associated with geochemical models.

7.4.3. Mean-annual Stable Isotope Compositions over the CGS

Using both data obtained from (Taylor 1990) and (Stewart et al. 2002), the weighted mean-annual isotopic composition of precipitation over Christchurch is -49 and -7.4 for δD and $\delta^{18}O$, respectively. Moreover, the calculated mean-annual *d* value is 9.8‰. These data agree marginally well (±1.0‰ for $\delta^{18}O$ and ±10‰ for δD) with a global model of -43 (±3‰) and 6.3 (±0.3‰) for δD and $\delta^{18}O$, respectively (Bowen, 2011; Bowen & Revenaugh, 2003). The modelled mean-annual *d* value from is 9.0‰, which is also ±10‰ of the observed 9.8‰. Similarly to monthly *d* values, the majority of precipitation, annually, originates from the Southern Pacific Ocean.

7.5. Surface/Groundwater Stable Isotope Compositions

7.5.1. Rainfall Infiltration Moisture Source

From Stewart et al. (2002), the weighted mean-annual $\delta^{18}O$ composition of lysimeter infiltration is -6.7‰, 0.7‰ more positive than the annual mean calculated for surface rainfall. It is unclear, at present, the reason for this positive shift. Also from Stewart et al. (2002), only

4 of 35 samples were analysed for both δH and $\delta^{18}O$, respectively. Although a limited dataset, the samples that were analysed for both elements plot very close to the Southern Pacific Ocean LMWL. This is best explained by rainfall infiltration generally being at its maximum potential in the winter months (White et al., 2003; Hong, 2005) which coincides with the average maximum monthly amounts for precipitation. As described in Section 7.4.2., winter precipitation is dominantly sourced from the Southern Pacific Ocean. On average, maximum infiltration occurs during the winter with considerably less infiltration occurring during the summer months (White et al., 2003; Hong, 2005). It therefore likely that subsequent lysimeter infiltration samples will plot along this LMWL, too.

7.5.2. Waimakariri River Water Source

$\delta^{18}O$ values for the Waimakariri River were obtained from the ECan Water Quality Database. Comparatively to monthly surface rainfall and rainfall infiltration, there is very little variation in the Waimakariri samples. This is largely explained by the 3 year residence time estimated from ^{3}H data (see Taylor et al. 1989), which dampens the intra-annual variations in the isotopic composition of precipitation falling in the catchment. The Waimakariri River flow is sustained by precipitation falling in the high-altitude sub-catchments located in the Southern Alps (Moore and Prowse, 1988). Precipitation falling in the Southern Alps is largely sourced from westerly mid-latitude cyclones and troughs from the Southern Pacific Ocean (Chater and Sturman, 1998; Moore and Prowse, 1988). However, low-pressure systems migrating southward from the northern Tasman Sea may also contribute significantly to precipitation falling in the Waimakariri Catchment. Notably, infrequent, high intensity precipitation events are associated with the low-pressure systems from the northern Tasman Sea. It is unclear which source region on average contributes the most volume of precipitation to the catchment.

The mean annual $\delta^{18}O$ value of the Waimakariri River has been calculated to be -9.6‰. The median $\delta^{18}O$ of the surface rainfall and lysimeter infiltration datasets are significantly different from that of the Waimakariri River ($p = < 0.0001$), however, *d* and $LMLW_{excess}$ values suggest that these water all originate from the similar source of the Southern Pacific Ocean. The differences in the $\delta^{18}O$ values are primarily resultant from both temperature and elevation isotopic effects associated with high-elevation precipitation in the Southern Alps (see Section 2.4.5. and Taylor et al., 1989).

Ultimately these differences in $\delta^{18}O$ are useful in determining recharge origins to groundwater systems.

7.6. Surface Water/Groundwater Interactions

7.6.1. Characterising Shallow Ground Recharge

Shallow groundwater recharge in the CGS is known to be sourced from rainfall infiltration over the study area and from river losses originating from the Waimakariri River. However, relative contributions of these 2 primary sources remain debated. A statistically robust end-member mixing model has previously not been implemented to investigate these processes or recharge volumes. (Taylor et al., 1989) estimated that from their observed $\delta^{18}O$ values, no more than 10% of groundwater losses to springs could be derived from precipitation. (Stewart et al., 2002) using a four part classification denoted the Avon River springs to be predominantly Waimakariri River derived, but with some addition of rainfall. Using a catchment water budget, White (2009) estimated rainfall infiltration to account for 20% of baseflow to the Avon River springs.

Using a binary single-element mixing model described by (Phillips and Gregg, 2001a), I quantified the relative contributions of the Waimakariri River to the Avon River springs. Error analysis was based on the intrinsic variability of end-member input compositions. The results of this model indicate that contributions to the Avon River are predominantly 80% sourced from the Waimakariri River, in accord with previous inferences by Taylor et al. (1989), Stewart et al. (2002), and White (2009).

In contrast, the modelling performed here incorporates the natural variability of isotopic compositions between end members. Thus, the original findings presented here likely better represent the surface/groundwater interactions associated with shallow groundwater recharge. However, to account for recharge throughout the CGS using geochemical methods, a more sophisticated (i.e. multi-end-member) and analytically precise (i.e. cavity-ring-down laser spectroscopy) survey of groundwater is needed. Furthermore, implementation of mixing models considering meteoric input must take into account the actual water, which infiltrates through the vadose zone as demonstrated here. The difference observed between using cumulative surface rainfall versus lysimeter infiltration may not always be relatively small.

Considering this dominance of Waimakariri River derived recharge to Aquifer 1 in the CGS, combined $\delta^{18}O$ isoscapes and hydrogeological potentiometric surfaces for shallow

groundwater in the CGS show distinct spatial patterns. More negative $\delta^{18}O$ values indicative of Waimakariri River channel leakage are observed both near the river and along the coastal boundary of the CGS. The latter has been interpreted as the upward flow of groundwater at depth in the presence of the artesian pressures from previous geochemical investigations (Talbot et al. 1986; Taylor & Fox 1996; Hanson & Abraham 2009). These patterns most likely emerge as a direct result of relict Waimakariri surficial floodplain deposits. These highly permeable "corridors" are likely associated with paleo-river channels of the anastomosing Waimakariri River (Soons et al., 1997; Bal, 1996; Leckie, 2003).

7.7. The CGS Water Budget and Deep Groundwater Flow Paths

7.7.1. High Groundwater Use, but No Declines

Water budgets are a simple mass-balance between inflows (recharge sources) and outflows (groundwater discharges) present in a hydrologic system, in this case, the CGS. Tables 7.1 and 7.2 present two water budgets for the CGS based on a compilation of recharge and discharge estimates from previous studies that differ based on recharge from the Waimakariri River. Scenario 1 considers groundwater recharge to the CGS to be strictly limited to the lower reaches of the Waimakariri River that are adjacent to the CGS, rainfall infiltration, and recharge from irrigation. However, Scenario 2 considers recharge from both the upper and lower reaches of the Waimakariri River, rainfall infiltration, and recharge from irrigation. For each scenario, groundwater outflows (discharge) remain the same.

Scenario 1	
Inflows (m^3/year)	**Outflows (m^3/year)**
Waimakariri River (lower reach) – 2.4×10^8	Abstractions – 1.06×10^8
Rainfall infiltration – 1.03×10^8	Avon River springs – 5.8×10^7
Recharge from irrigation – 3.5×10^6	Heathcote River – 3.1×10^7
	South Branch – 9.5×10^7
	Styx River – 5.1×10^7
	Ocean discharge – 3.1×10^7
TOTAL – 3.4×10^8	**TOTAL – 3.7×10^8**
Net loss of 0.3×10^8	

Table 7.1: Inflows and outflows with respect to the CGS considering losses from the lower Waimakariri River only (Scott and Thorley, 2009; Talbot, 2010; Talbot et al., 1986)

Scenario 2	
Inflows (m^3/year)	**Outflows (m^3/year)**
Waimakariri River (upper reach) – 9.5×10^7	Abstractions – 1.06×10^8
Waimakariri River (lower reach) – 2.4×10^8	Avon River springs – 5.8×10^7
Rainfall infiltration – 1.03×10^8	Heathcote River – 3.1×10^7
Recharge from irrigation – 3.5×10^6	South Branch – 9.5×10^7
	Styx River – 5.1×10^7
	Ocean discharge – 3.1×10^7
TOTAL – 4.4×10^8	**TOTAL – 3.7×10^8**
Net gain of 1.3×10^8	

Table 7.2: Inflows and outflows with respect to the CGS considering losses from the Waimakariri River both from the upper and lower reaches (Scott and Thorley, 2009; Talbot et al., 1986; Talbot, 2010)

Under Scenario 1, the CGS would be losing approximately 109 % of its total annual recharge to outflows. Interestingly, no significant declines in water levels have been observed since the mid-20th century (Brown, 2001). Under Scenario 2, the CGS would be losing approximately only 85 % of its total annual recharge. Scenario 2 fits a model in which the observation large abstractions of groundwater occur from the CGS, but declines in groundwater levels are not observed as there has been not net loss to groundwater system. However, this would entail that groundwater would be entering into the CGS from Central Canterbury Plains (shallow, deep, or some combination of groundwater) in some manner, which is outside the management zone.

Taylor & Fox (1996) estimated the ages for deep groundwater on the order of 2,500 to 3,500 years old in the CGS. However, these ages are not compatible with estimated aquifer volumes, abstraction rates, and observed water levels (Scott and Thorley, 2009; Talbot et al., 1986; Talbot, 2010). Moreover, the aquifer storage volume required to accommodate these residence times is ten times larger than what is estimated (Taylor and Fox, 1996). Ultimately, the questions remain: what is the source of the water recharging the aquifers?

7.7.2. Limits of a $\delta^{18}O$ mixing model

Rainfall infiltration over the CGS shows a distinct difference with respect to alpine derived precipitation (p = <0.0001), however $\delta^{18}O$ compositions of rainfall infiltration become increasingly more negative inland (Stewart et al., 2002). At the Hororata site (see Stewart et al.), the mean annual $\delta^{18}O$ composition of precipitation was observed to be -9.5‰ in contrast to the -7.4‰ at Christchurch International Airport. A simple single-isotope mixing model would therefore be unable to resolve any difference between the Waimakariri River derived recharge versus rainfall infiltration near the foothills of the Southern Alps, as both are very similar with respect to their mean $\delta^{18}O$ values.

7.7.3. Deep groundwater flow

Weir (2007) presents a regionally developed model for groundwater flow in the Central Canterbury Plains, including the CGS that, at depth, shows flow paths originating from both the Waimakariri River and the Central Canterbury Plains for March 1994. These observations would agree with the apparent 35 meter drop in groundwater levels from the Central Canterbury Plains to the CGS near Banks Peninsula in Aquifer 4 measured during September 2003 (Weir 2007). These patterns are also interpreted from potentiometric surfaces calculated for the average groundwater level for 2006 to 2010. Furthermore, despite the ranges in groundwater levels for these wells, the observed groundwater flow paths from the Central Canterbury Plains to the CGS are still observed. Lastly, backwards modelling show multiple wells released from the western margin of the CGS to originate from the much farther into the Central Canterbury Plains outside the CGS (Weir, 2007). Based on these observations, some component of deep groundwater from the Central Canterbury Plains is contributing to recharge of the CGS.

Deep groundwater in the CGS may not be entirely derived from the Waimakariri River. A significant component of "recharge" to the deeper aquifers in the CGS may come as groundwater movement from the Central Canterbury Plains as evidenced by both physical groundwater models and observed potentiometric gradients. Groundwater movement from the Central Canterbury Plains to the CGS could provide one explanation as to why no observable declines have been noticed in the CGS groundwater levels despite abstracting more than its annual recharge if recharge is solely within the management zone. More sophisticated geochemical models are needed to characterize deep groundwater derived from foothills infiltration as $\delta^{18}O$ values for mean annual precipitation (-9.6 ‰) near the foothills are very similar to the mean annual Waimakriri River value (-9.6 ‰) (Stewart et al. 2002).

7.8. Summary

The stable isotope variability of precipitation events over Christchurch, New Zealand is relatively large ($\delta^{18}O$ > 20‰). Isotopic compositions of precipitation events are linked to both kinetic fractionation effects during water vapour formation and surface meteorological conditions during collection. Derived LMWLs based on back-trajectory analysis exhibit *d* values closely associated with environmental conditions present from their respective moisture sources. Tropical and sub-tropical sourced precipitation generally exhibit precipitation with low *d* values characteristic these regions where evaporation rates and relatively humidity are high. Mid-latitude sourced precipitation from the Southern Pacific Ocean plots closer to the GMWL and furthermore, its *d* values are characteristic of moisture sourced from lower relatively humidity as evidenced by its more positive *d* values.

Tropical cyclone events support these distinctions of moisture sources. As the low pressure systems migrate southward, moisture is progressively sourced from tropical to sub-tropical to mid-latitude sources. Coinciding with these changes is a positive shift in *d* values as would be expected. The most negative $\delta^{18}O$ value is associated with the onset of a tropical cylone. Furthermore, many of the negative isotopic compositions in the dataset are associated with extra-tropical depressions. However, resolving these anomalous inputs in hydrologic systems in unlikely over longer time-scales or in well mixed systems.

The isotopic composition of monthly precipitation exhibits seasonal trends with respect to $\delta^{18}O$ and *d* that are attributed to seasonal changes in atmospheric circulation. A significant difference is observed between the median $\delta^{18}O$ values of monthly precipitation and the Waimakariri River and between rainfall infiltration and the Waimakariri River. This observation is important in potentially quantifying recharge amounts based on a linear mixing model. Deuterium excess values suggest that water occurring over the CGS and the Southern Alps (the Waimakariri River catchment), the predominant atmospheric source of moisture comes from the Southern Pacific Ocean. These similarities, however, do not make *d* an ideal tracer for surface and groundwater interactions.

Calculation of relative contributions to the Avon River springs using the single-isotope mixing model suggest 80% of the Avon River springs' baseflow to derived from rainfall infiltration. This observation agrees well with previous estimates; however this is the first study to consider the variability of input end-members.

Spatial distributions in $\delta^{18}O$ values in the groundwater system are related to the surficial geology associated with the Waimakariri River Floodplain. At depth, $\delta^{18}O$ values in groundwater become more negative, however, flow paths appear to increasingly flow more from the Central Canterbury Plains into the CGS as documented from previous studies and original work in this thesis

Current geochemical models are unable to resolve the amount of deep groundwater from the Central Canterbury Plains that contributes to the CGS, however these contributions likely account for the inflows needed to offset the negative losses a CGS water budget that only considers inflows from the lower Waimakariri River reaches and rainfall infiltration.

Chapter 8 : Conclusions and Future Research Directions

8.1. Conclusions

The isotopic composition of Christchurch precipitation is highly variable. These variations are due in part to the complex oceanic-atmospheric processes present around New Zealand. However, distinct local meteoric waterlines are derived from specific moisture origins (i.e. Southern Pacific Ocean, Tasman Sea, and the Tropical Pacific) from back-trajectory analysis. Differences in these local meteoric water lines are associated with the kinetic fractionation effects largely controlled by the environmental conditions during water vapour formation from the respective moisture sources. These differences are evidenced by large shifts in the deuterium excess values in intra-storm samples from two extra-tropical cyclone events.

Monthly surface rainfall, rainfall infiltration, surface waters, and groundwater show the least amount of deviations from the Southern Pacific Ocean local meteoric water line. This suggests the predominant moisture source to Christchurch to be largely derived from south-south westerly flow and contributed moisture from the Southern Pacific Ocean. These observations, however, do not serve as a good indicator between surface water and groundwater interactions.

There is a statistically significant difference between $\delta^{18}O$ of surface rainfall and rainfall infiltration and the Waimakariri River. Using a binary mixing model, contributions from the Waimakariri River to the Avon River springs showed that the Waimakariri River accounted for approximately 80% of recharge. These findings also agree well with a previous physical water budget for the Avon River springs.

At depth, $\delta^{18}O$ values generally decrease, which has been attributed to increasing dominance of recharge from the Waimakariri River. However, potentiometric surfaces generated for this thesis, previous potentiometric surfaces, and backwards groundwater flow path modelling all show in the southern portion of the CGS, groundwater appears to flow from the Central Canterbury Plains to the CGS. $\delta^{18}O$ values, alone, would not be able to resolve this problem as contributions from the upper reaches of the Waimakariri and surface infiltration are very similar in their $\delta^{18}O$ values.

8.2. Future Research Directions

Monitoring of the stable isotopic composition of precipitation, surface waters, and groundwaters for both $\delta^{18}O$ and δD is needed for the Canterbury region. Future geochemical models should attempt more species for a more robust mixing model that could potentially differentiate between shallow groundwater losses from the Waimakariri River and contributions to the CGS from Banks Peninsula, sea-water intrusion, and potentially, from the Central Canterbury Plains.

The CGS is a complex groundwater system that, at present, cannot be fully explained by either stable isotope or physical hydrological investigations. However, future research should seek to combine observations from both approaches to validate determinations of groundwater processes that will ultimately better inform water resource managers of the Canterbury region.

Chapter 9 : Bibliography

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Chapter 10 : Appendices

Appendix 1

Isotope Effect	Description
Altitude (elevation)	Adiabatic lifting of air masses cause cooling and condensation to occur and subsequent precipitation. Progressive depletion of isotopic composition incurs with the continual "uplift" and of preference of heavier isotopes for the liquid phase in subsequent precipitation. An example of this can be seen in the change in isotopic composition across mountain belts.
Amount	The amount effect is an observed negative correlation between the amount of precipitation occurring at a given location and the subsequent isotopic composition. The amount effect is more commonly observed in tropical regions. With higher latitudes, this relationship is not commonly observed. As previously mentioned, heavier isotopes preferentially rainout from air masses, however, this simple explanation does not explain larges variations associated with complex in-cloud processes and climatological factors that do ultimately affect the isotopic composition of subsequent precipitation
Continental (distance)	Continual passage of air masses over continental regions generally result in the progressive depletion of heavier isotopes as these air masses move farther from their moisture source (Sharp, 2007). Modification of air mass isotopic composition do incur from mixing of water vapour sourced from continental sources (i.e. Great Lakes, North America).
Latitude	Global circulation patterns, such as Walker and Hadley circulation, generate a progressive movement of moisture advected from equatorial regions to higher latitudes. The progressive movement of air masses is associated with both decreased temperatures and resultant precipitation. Subsequently, these two factors contribute to more negative isotopic compositions in air masses and subsequent precipitation
Seasonal	Seasonal shifts in the isotopic composition of precipitation may be attributed to both local changes in temperature and shifts in the predominant moisture origin of rainfall. The latter encompassing an associated temperature effect for moisture sources. This

	observation is seen globally and with increased latitudes and distances inland, the magnitude of seasonal variation generally increases .
Temperature	The ability of air masses to hold water (residual vapour fraction) is a function of air temperature and from Dansgaard (1964), as vapour fraction decreases, so does the isotopic composition ratio.

Appendix 2 – See attached CD

Appendix 3 – See attached CD